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6 hours with potassium hydroxide, sodium ethoxide, or potassium phthalimide, respectively. Displacement was not detected in a 4*N*-sulphuric acid solution which had been kept for weeks at laboratory temperature. The simultaneous formation of a nitrosoamine did not occur. In this respect, as also in the production of free halogen, *p*-iododimethylaniline differs from *p*-chloro- or *p*-bromo-dimethylaniline (compare Wurster and Scheibe, *Ber.*, 1879, **12**, 1816; Heidlberg, *Ber.*, 1887, **20**, 149; Koch, *ibid.*, p. 2460; Pinnow, *Ber.*, 1898, **31**, 2984).

The bromonitrodimethylaniline, m. p. 67·5°, isolated by Koch is readily obtained also by bromination of 2-nitrodimethylaniline in glacial acetic acid at 60°, and is probably 4-bromo-2-nitrodimethylaniline. The orientation given for the iodonitrodimethylaniline, m. p. 60—60·5°, is probable because its hydrochloride is precipitated immediately when ethereal solutions of iodine monochloride and 2-nitrodimethylaniline are mixed at 15°.

Iododimethylaniline of m. p. 79·5° (Weber, *Ber.*, 1877, **10**, 765; Reade and Sim, J., 1924, **125**, 158) has also been formed from *p*-nitrosodimethylaniline by reduction, diazotisation, and introduction of iodine, to prove that it is the para-compound.

p-Iododimethylaniline (1/10 mol.) in 80 c.c. of 4*N*-sulphuric acid was slowly run into silver nitrite (1/10 mol.) in ½ l. of water at 18° (alternatively into aqueous sodium nitrite, when iodine separated). After 1 hour's shaking, digestion of the precipitate with hot alcohol, filtration, and concentration, 6—7 g. of greenish-brown crystals were obtained. These were separated by fractional crystallisation from absolute alcohol into *p*-nitrodimethylaniline, melting, alone or mixed with an authentic specimen, at 163°, and a more soluble, less abundant fraction, consisting of orange needles of *4-iodo-2-nitrodimethylaniline*, m. p. 60·5° (Found : C, 33·0; H, 1·9; N, 11·0; I, 43·5. $C_8H_9O_2N_2I$ requires C, 32·9; H, 3·1; N, 9·6; I, 43·5%).

o-Nitrodimethylaniline sulphate, prepared by Weissenberger's method (*Monatsh.*, 1912, **33**, 821) and crystallised from alcohol, melted at 168° (Weissenberger gives m. p. 126—127°). When a dried ethereal solution of the base obtained from 9·3 g. of the sulphate was treated with 5·4 g. of iodine monochloride at 15°, 4-iodo-2-nitrodimethylaniline hydrochloride was rapidly precipitated. The corresponding base crystallised from absolute alcohol in orange needles, m. p. 60—60·5°, alone or mixed with the specimen described above.

The authors thank the United Alkali Company for a gift of *o*-chloronitrobenzene.—University of Aberdeen. [*Received, April 26th*, 1926.]

The Alleged Decomposition of Aqueous Ammonium Nitrite Solutions by Light. By MARSHALL HOLMES.

WHEN a 2·5*N*-solution of ammonium nitrite (smelling of ammonia, but free from nitrate) was insolated in a quartz flask by means of a 110-volt Cooper-Hewitt quartz-mercury lamp at a distance of 8—16 cm., no loss of nitrite could be detected even after 6 hours, titration with *N*/10-potassium permanganate being the analytical method employed. If the insolation was continued up to 100 hours, slight losses were detected, but these were due entirely to thermal decomposition, since similar "dark" control solutions suffered the same loss within the limits of experimental error.

In the foregoing experiments the temperature of the solution had been kept at 22° ± 1° by the circulation of tap water round the reaction vessel. As this method of cooling led to slight and variable absorption of ultra-violet light by the water, another apparatus was devised wherein such absorption was eliminated. After 9 hours at 20° ± 0·1° at a distance of 15 cm., titrations showed almost the same decomposition as in the "dark" solution:

Original solution required	21·70 c.c.
Solution after 9 hours' insolation required . . .	21·16 c.c.
„ „ „ „ in dark „ . . .	21·19 c.c.

It is therefore concluded that Berthelot and Gaudechon (*Compt. rend.*, 1911, **152**, 522) were in error in stating that nitrogen was evolved as a result of insolating ammonium nitrite. As they gave but scanty details of their experimental procedure, however, it is impossible to determine the cause of disagreement, but it is probable that, as no mention is made of control experiments in the dark, they omitted this precaution and were, in fact, observing a purely thermal reaction. In the same paper, they record temperatures of 35—50° as being reached when studying other photo-reactions.

The author is indebted to Professor Allmand for suggesting this work, and to the Department of Scientific and Industrial Research for a grant which enabled him to carry it out.—KING'S COLLEGE, UNIVERSITY OF LONDON. [*Received, April 28th*, 1926.]

The Temperature of Maximum Density of Alcohol–Water Mixtures. By JOHN P. MCHUTCHISON.

ACCORDING to Despretz (*Ann. Chim. Phys.*, 1839, **70**, 49; 1840, **73**, 296) the lowering of the temperature of maximum density of water caused by the addition of a soluble salt is directly proportional to the concentration of the solute (Despretz's law). It

appears, however (see Coppet, *ibid.*, 1903, **28**, 12; Wright, J., 1919, **115**, 119), that feebly ionised or non-ionisable substances do not obey Despretz's law, and even that ethyl alcohol in certain concentrations causes an elevation of the temperature of maximum density.

The behaviour of five alcohols has now been investigated with Wright's apparatus (*loc. cit.*), and the following results have been obtained:

TABLE.

Temperatures of Maximum Density of Alcohol–Water Mixtures.

Alcohol.	2*M*.	*M*.	*M*/2.	*M*/4.	*M*/8.	*M*/16.
Methyl	1·90°	3·65°	3·95°	4·00°	4·00°	—
Ethyl	0·15	3·70	4·25	4·20	4·15	—
n-Propyl	—	1·50	3·30	3·80	4·15	4·10°
*iso*Propyl	—	2·65	3·70	4·00	4·00	—
n-Butyl	—	—	—	3·10	3·90	3·90

(Temperature of maximum density of pure water as determined by the apparatus employed, 4·00°.)

It is clear (1) that in none of these cases is there proportionality between the lowering of the maximum-density temperature and the alcohol concentration, and (2) that, besides ethyl alcohol, *n*-propyl alcohol alone gives rise to an elevation of the temperature of maximum density.—GLASGOW UNIVERSITY. [*Received, May* 14*th*, 1926.]

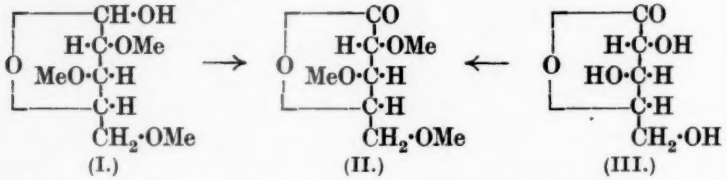
CCL.—*The Structure of Lactones from Simple Sugars. Trimethyl γ-Arabonolactone and the Supposed β-Gluconolactone and β-Mannonolactone.*

By WALTER NORMAN HAWORTH and VINCENT STANLEY NICHOLSON.

CONTINUING the work described in the communication on "A Revision of the Structural Formula of Glucose" by Charlton, Haworth, and Peat (this vol., p. 89), the present authors have prepared γ-arabonolactone from *l*-arabinose as indicated by Fischer and Piloty (*Ber.*, 1891, **24**, 4214) and Nef (*Annalen*, 1914, **403**, 204) and have isolated, by methylation of this lactone, the corresponding trimethyl γ-arabonolactone. This had previously been isolated by Baker and Haworth (J., 1925, **127**, 365) by the method of oxidising trimethyl γ-arabinose with nitric acid, and the identity of the two specimens is established by the following comparison of their properties:

	Trimethyl γ-arabonolactone from trimethyl γ-arabinose.	Trimethyl γ-arabonolactone from γ-arabonolactone.
Crystalline form	Long, colourless needles.	Long, colourless needles.
M. p.	32°	33° (and mixed m. p. 33°)
$[\alpha]_D$ in water, initial	−43·2°	−44·4°

This result confirms the constitution assigned by Baker and Haworth to trimethyl γ-arabinose (I), since the derived lactone (II) is identical with the product obtained by methylating the stable or γ-arabonolactone (III).



(I.) (II.) (III.)

Nef (*loc. cit.*) outlined improved methods of preparing the ordinary stable γ-lactones from sugars, and suggested that simultaneously with the formation of these stable forms other lactones of a less stable character were also produced in varying but much smaller quantity. By a considerable modification of method, involving carefully graduated heating of the hydroxy-monocarboxylic acids over a prolonged period, or by low-temperature treatment in a vacuum, he succeeded in preparing, and isolating from their stable forms, two of these unstable lactones, which he described as β-gluconolactone and β-mannonolactone, the properties of which are given below for comparison with the predominant or stable γ-forms :

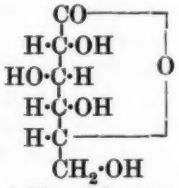
	γ-Gluconolactone.	"β"-Gluconolactone.
M. p.	133—135°	150—152°
$[\alpha]_D$ in water	+67·82° (little change in 22½ hours)	+61·7° ⟶ 6·24° (in 26 hours)

	γ-Mannonolactone.	"β"-Mannonolactone.
M. p.	151°	156°
$[\alpha]_D$ in water	+51·8° (no change in 4 days)	+111·1° ⟶ 28·08° (in 24 hours)

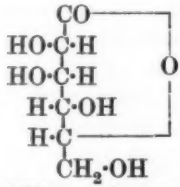
Nef regarded the isolation of these two types of lactones as evidence of the structural rather than the stereochemical isomerism of α- and β-glucoses and of α- and β-methylglucosides, an inference which was strongly resisted by E. Fischer (*Ber.*, 1914, **47**, 1980). This unfortunate application of Nef's results has tended to obscure the real significance of the isolation of isomeric crystalline lactones from glucose and mannose.

We are of opinion, however, for the following reasons, that the unstable forms of glucono- and mannono-lactones are not β-lactones

as supposed by Nef, but are in reality δ-lactones, containing a six-membered ring (1 : 5 oxide) corresponding to the normal or amylene-oxidic form of the parent sugars. If these were indeed β-lactones, then the lactone ring would be formed by engaging in each case hydroxyl groups on the left of the carbon chain and thus by Hudson's rule (*J. Amer. Chem. Soc.*, 1910, **32**, 345) the lactones should be lævorotatory or more lævorotatory respectively than gluconic or mannonic acid. This is not the case, since the rotations are strongly dextro and decline markedly to constant dextro values in 24 hours. The rotation changes, quoted in detail by Nef, are indeed comparable in all respects with those indicated in the graph published by Charlton, Haworth, and Peat (*loc. cit.*) for δ-lactones, and the figures given by Nef enable similar curves to be drawn which prove the similarity in behaviour to tetramethyl δ-gluconolactone, tetramethyl δ-galactonolactone, and trimethyl δ-arabonolactone (compare also the figures given for the corresponding tetramethyl δ-mannonolactone). We therefore assign the following structural formulæ to Nef's lactones:



δ-Gluconolactone.



δ-Mannonolactone.

If the usual method for the conversion of gluconic and mannonic acids into their lactones be adopted, the yield of the above unstable varieties would appear to be exiguous, and until 1914 the occurrence of these forms was unsuspected. The predominating lactone is invariably of the γ-type even in solution (compare Levene and Simms, *J. Biol. Chem.*, 1925, **65**, 31).

In discussing the formation of the lactone from 2 : 3 : 6-trimethyl gluconic acid, Charlton, Haworth, and Peat indicated for the above reasons that the choice was restricted to the γ-lactone by Hudson's hypothesis. We believe, however, that under experimental conditions resembling those described by Nef for the preparation of unstable lactones it will also be possible to isolate the 2 : 3 : 6-trimethyl δ-gluconolactone which, on methylation, should be identical with the lactone derived from normal tetramethyl glucose, and with the product obtained on methylating Nef's supposed " β "-gluconolactone, and this investigation is in progress.

Nef regarded the stable γ-lactones as the abnormal type, and the unstable lactones (δ-) as the normal variety. This accords with our

views, since we consider the former to be related to the γ-aldoses and the latter to the normal aldoses of the pentose and hexose series.

Experimental.

Methylation of γ-Arabonolactone.—*l*-Arabinose was oxidised by bromine water to γ-arabonolactone following the conditions outlined by Kiliani (*Ber.*, 1886, **19**, 48; compare also Fischer and Piloty, Nef, *loc. cit.*). The lactone was methylated several times by Purdie's reagents, initially in presence of methyl alcohol and latterly with methyl iodide and silver oxide alone (Found : OMe, 51·8. Calc. : OMe, 48·9%). It was ascertained that this high methoxyl content was due to the presence of the corresponding methyl ester. The lactone was therefore purified by formation of the sodium salt in the cold, and the solid obtained on evaporation was extracted with warm ether. Thereafter an aqueous solution of the salt was acidified, evaporated to dryness under diminished pressure, and the resulting organic acid was extracted and heated at 100° for several hours in order to regenerate the lactone. Distillation of the latter at a bath temperature of 115° under 0·015 mm. pressure gave a colourless liquid which completely crystallised (m. p. 26—27°) on nucleation with a specimen of the trimethyl arabonolactone prepared by Baker and Haworth (*loc. cit.*). After being kept on porous tile in a desiccator, the crystals melted at 33°, and the m. p. was unchanged by recrystallisation of the substance from light petroleum. Baker and Haworth's specimen, originally quoted as m. p. 29°, was kept over phosphoric oxide in a vacuum and then melted at 32°. A mixture of the two specimens melted at 33° (Found : C, 50·6; H, 7·6; OMe, 46·3. Calc. : C, 50·5; H, 7·4; OMe, 48·9%). The specific rotation values in water ($c = 1·06$) were $-44·4°$, after 5 mins.; 44·3°, 30 mins.; 44·1°, 1 hour; 43·8°, 2 hours; 43·4°, 4 hours; 40·0°, 24 hours.

University of Birmingham,
Edgbaston.

[*Received, May 1st*, 1926.]

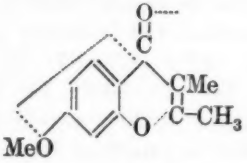
CCLI.—*Styrylbenzopyrylium Salts. Part VII. The Conversion of 7-Methoxy-2 : 3-dimethylchromone into Styrylpyrylium Salts.*

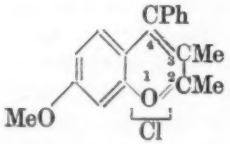
By Isidor Morris Heilbron and Ahmad Zaki.

It has been shown by one of us (J., 1923, **123**, 2559) that the reactivity of the 2-methyl group in 2 : 3-dimethylchromone is completely inhibited by suitable substitution in the benzene ring. For

example, 7-methoxy-2 : 3-dimethylchromone fails to condense with aromatic aldehydes to form styryl derivatives, and this failure has been attributed to a complete neutralisation of the partial valency forces (I). In this compound, the carbonyl group may be regarded as the essential primary centre of activity and consequently its removal should enable the characteristic reactivity of the 2-methyl group to be re-established. In order to test this point, 7-methoxy-2 : 3-dimethylchromone has been converted into *7-methoxy-4-phenyl-2 : 3-dimethylbenzopyrylium chloride* (II) as detailed in the experimental part. This salt possesses extraordinary activity, condensing rapidly with aromatic aldehydes in alcoholic solution, without the presence of any catalyst, to yield 2-styrylbenzopyrylium salts. In this respect, it is analogous to 1-ethyl-2-methylene-1 : 2-dihydroquinoline in its condensation with *p*-dimethylaminobenzaldehyde (Mills and Raper, J., 1925, **127**, 2466) and is more active than the similarly constituted 7-hydroxy-2-phenyl-4-methylbenzopyrylium chloride, which requires the presence of dry hydrogen chloride to bring about condensation (Buck and Heilbron, J., 1923, **123**, 2521).

(I.)





(II.)

Owing to the ease with which the Grignard reagent reacts with the chromone, the opportunity has been taken of studying the effect of introducing auxochromic groups into the substituting phenyl group in position 4. This has been found to produce a decided influence on the colour of the salts; *e.g.* the unsubstituted salt (II) is yellow and dissolves in alcohol to an intensely yellow solution, the 4-*anisyl* derivative is orange and gives red to brown solutions, whilst *7-methoxy*-4-p-*dimethylaminophenyl*-2 : 3-*dimethylbenzopyrylium chloride*, containing the more powerful auxochromic dimethylamino-group, separates in microscopic reddish-purple needles which dissolve in alcohol with an intense purple colour. The styrylbenzopyrylium salts are, in general, similar in their properties to the γ-styryl derivatives (Buck and Heilbron, J., 1923, **123**, 2521). They differ from these, however, in their more ready solubility and in the ease with which they yield the carbinol bases. All the styrylbenzopyrylium chlorides of this series crystallise from solvents with indefinite addenda, and for analysis the *ferrichlorides* or *perchlorates* were invariably employed.

Experimental.

7-Methoxy-4-phenyl-2 : 3-dimethylbenzopyrylium Chloride (II).—7-Methoxy-2 : 3-dimethylchromone (10 g.) was dissolved in carefully dried benzene (100 c.c.) and treated in the heat with a concentrated solution of magnesium phenyl bromide (2 mols.). The yellow solution was heated under reflux for 1½ hours and, after cooling, decomposed with concentrated hydrochloric acid (50 c.c.), added in small portions at a time; the pyrylium chloride was thus precipitated in quantitative yield. It separated from dilute hydrochloric acid in long, yellow needles which contained indefinite addenda together with a small quantity of some magnesium complex. The chloride was therefore dissolved in aqueous alcohol and treated with dilute ammonium hydroxide solution. The colourless carbinol base was extracted with ether, and the chloride reprecipitated by saturating the dried ethereal solution with dry hydrogen chloride. The *ferrichloride*, prepared by heating together ferric chloride and the pure chloride in glacial acetic acid, separated from acetone–light petroleum in large, greenish-yellow needles, m. p. 114°, freely soluble in alcohol and acetone, but insoluble in ether and benzene (Found: C, 46·7; H, 3·7; Cl, 30·7; Fe, 12·1. $C_{18}H_{17}O_2Cl_4Fe$ requires C, 46·7; H, 3·6; Cl, 30·8; Fe, 12·1%). The *perchlorate*, prepared by the addition of 20% perchloric acid to a solution of the chloride in alcohol, crystallised from alcohol containing perchloric acid in orange-yellow needles, m. p. 206°, readily soluble in hot water, alcohol, and glacial acetic acid (Found: C, 59·2; H, 4·7. $C_{18}H_{17}O_6Cl$ requires C, 58·9; H, 4·9%).

7-Methoxy-4-phenyl-2-p-hydroxystyryl-3-methylbenzopyrylium chloride was prepared by gently boiling a solution of the crude parent chloride (6 g.) and *p*-hydroxybenzaldehyde (2·4 g.) in methyl alcohol (18 c.c.). The solution rapidly became deep red and on cooling in the ice-chest the whole set to a crystalline mass. The salt was purified by regeneration from the colour base and separated from methyl alcohol containing a few drops of concentrated hydrochloric acid in glistening, brick-red crystals, m. p. 275° (decomp.). On treating an aqueous-alcoholic solution with dilute aqueous sodium hydroxide, a blue solution is formed from which the colour base is rapidly precipitated, but this, on being shaken with more alkali, passes into the carbinol base. The *perchlorate* separates from either glacial acetic acid or dilute alcohol containing perchloric acid in red needles (Found: C, 64·0; H, 4·6. $C_{25}H_{21}O_7Cl$ requires C, 64·0; H, 4·5%).

7-Methoxy-4-phenyl-2-p-methoxystyryl-3-methylbenzopyrylium chloride was obtained, after two recrystallisations from alcoholic hydro-

chloric acid, in red needles, soluble in cold water to a red solution which on treatment with alkali immediately yields the carbinol base. The *ferrichloride* forms brick-red needles (Found: C, 53·7; H, 4·1; Fe, 9·8. $C_{26}H_{23}O_3Cl_4Fe$ requires C, 53·7; H, 4·0; Fe, 9·7%).

7-*Methoxy*-4-*phenyl*-2-p-*hydroxy*-m-*methoxystyryl*-3-*methylbenzopyrylium chloride*, prepared from the crude parent chloride and purified through the colour base, separates from dilute alcohol containing hydrochloric acid in glistening, dark green crystals, soluble in dilute hydrochloric acid, alcohol and glacial acetic acid to deep-red solutions. The alcoholic solution changes to deep blue on addition of aqueous sodium hydroxide. The *ferrichloride* forms dark green needles readily soluble in water, alcohol, or acetone (Found: C, 51·9; H, 4·1; Fe, 9·5. $C_{26}H_{23}O_4Cl_4Fe$ requires C, 52·3; H, 3·9; Fe, 9·4%).

7-*Methoxy*-4-*phenyl*-2-p-*dimethylaminostyryl*-3-*methylbenzopyrylium Chloride*.—7-Methoxy-4-phenyl-2 : 3-dimethylbenzopyrylium chloride (5 g.) was dissolved in boiling alcohol (20 c.c.), and *p*-dimethylaminobenzaldehyde (2·5 g.) added to the hot solution, the colour instantly changing to olive-green. The mixture was heated for 10 minutes on a water-bath and, on cooling, solidified to a bright green, crystalline mass. The salt separates from alcohol in green crystals easily soluble in acidified water to a green solution which on high dilution changes to blue. It is readily soluble in alcohol, acetone, or chloroform, giving deep blue solutions. When an alcoholic solution of the chloride is treated with a few drops of aqueous potassium hydroxide, a colourless solution is formed from which, on addition of water, the colourless carbinol base is precipitated. Sodium acetate precipitates the anhydro colour base as a violet precipitate. The *ferrichloride* crystallises from acetone in green crystals (Found: C, 54·4; H, 4·4; Fe, 9·4. $C_{27}H_{26}O_2NCl_4Fe$ requires C, 54·5; H, 4·4; Fe, 9·4%). The *diperchlorate*, obtained in yellow crystals by treating the chloride with boiling perchloric acid, passes on treatment with solvents into the *monoperchlorate*, which forms dark bluish-green crystals (Found: C, 65·2; H, 5·5. $C_{27}H_{26}O_6NCl$ requires C, 65·4; H, 5·2%).

7-*Methoxy*-4-p-*anisyl*-2 : 3-*dimethylbenzopyrylium chloride* was prepared by treating 7-methoxy-2 : 3-dimethylchromone with magnesium *p*-anisyl bromide. It crystallises from alcohol in orange-yellow needles, m. p. 160°, readily soluble in dilute hydrochloric acid, alcohol, or glacial acetic acid. The *ferrichloride* separates from absolute alcohol in orange-yellow crystals (Found: C, 46·1; H, 4·1; Fe, 11·3; Cl, 29·1. $C_{19}H_{19}O_3Cl_4Fe$ requires C, 46·2; H, 3·9; Fe, 11·3; Cl, 28·8%).

7-*Methoxy*-4-p-*anisyl*-2-p-*hydroxystyryl*-3-*methylbenzopyrylium chloride* crystallises from alcohol in red needles which behave in an exactly similar manner to the 4-phenyl analogue. The *ferrichloride* forms red needles (Found : C, 51·9; H, 4·0; Fe, 9·4. $C_{26}H_{23}O_4Cl_4Fe$ requires C, 52·2; H, 3·9; Fe, 9·4%).

The corresponding p-*methoxy-chloride* forms long, red needles soluble in alcohol to a red solution from which the carbinol base is precipitated on addition of dilute aqueous sodium hydroxide. The *ferrichloride* forms brownish-red needles (Found : C, 52·7; H, 4·3; Fe, 9·1. $C_{27}H_{25}O_4Cl_4Fe$ requires C, 53·0; H, 4·1; Fe, 9·2%).

7-*Methoxy*-4-p-*anisyl*-2-p-*dimethylaminostyryl*-3-*methylbenzopyrylium chloride* separates from absolute alcohol in olive-green crystals with an intense bronze sheen. Its behaviour with alkali and sodium acetate is exactly analogous to that of the 4-phenyl analogue. The *ferrichloride* crystallises from acetone in green needles, m. p. 125° (Found : C, 53·6; H, 4·8; Fe, 9·1. $C_{28}H_{29}O_3NCl_4Fe$ requires C, 53·8; H, 4·6; Fe, 9·0%).

7-*Methoxy*-4-p-*dimethylaminophenyl*-2 : 3-*dimethylbenzopyrylium chloride* was prepared by the interaction of 7-methoxy-2 : 3-dimethylchromone with magnesium *p*-dimethylaminophenyl iodide. A deep brown colour at once developed and the reaction was completed by boiling the mixture for an hour on the water-bath. When cold, the liquid portion was decanted and decomposed with concentrated hydrochloric acid. The pyrylium chloride, which separated as a deep purple oil, was taken up in a very small quantity of boiling absolute alcohol and, after vigorous scratching, crystallised in dark olive-green crystals giving a purple streak on paper. It is sparingly soluble in water, readily so in alcohol, to purple-red solutions. With dilute hydrochloric acid, a yellow solution is formed which, on large dilution with water, changes to purple-red. The *perchlorate*, obtained through the colourless carbinol base, crystallises from glacial acetic acid in dark purple needles readily soluble in alcohol or glacial acetic acid (Found : C, 58·6; H, 5·5. $C_{20}H_{22}O_6NCl$ requires C, 58·9; H, 5·4%). Condensations of this pyrylium salt were carried out and although styryl derivatives were undoubtedly formed, these separated as oils which could not be induced to crystallise.

The authors desire to thank Mr. H. Dale, B.Sc., for valuable assistance in this investigation.

THE UNIVERSITY, LIVERPOOL. [*Received, May 29th*, 1926.]

CCLII.—*The Viscosities and Densities of Anhydrous Methyl Alcohol and of Solutions of some Halides of Sodium and Potassium in this Solvent.*

By Frederick Kenneth Ewart and Humphrey Rivaz Raikes.

The work detailed in this paper forms part of an investigation of the properties of solutions of electrolytes in methyl alcohol which is being carried on in this laboratory.

Although there are several values for the density of the pure solvent to be found in the literature, there are no data concerning the densities of solutions of electrolytes in methyl alcohol. Values for the viscosity of the pure alcohol are notably those of Dunstan (J., 1914, **105**, 784) and of Thorpe and Rodger (*Phil. Trans.*, **1894**, *A*, **185**, 531). The only previous systematic work on the viscosities of halide solutions is that of Tower (*J. Amer. Chem. Soc.*, **1916**, **38**, 833).

Experimental.

The preparation of the pure alcohol is described by Hartley and Raikes (J., 1925, **127**, 524). The only departure from their procedure was that the present authors avoided the use of drying agents altogether, relying entirely on repeated fractionation under the most careful conditions. It was shown by determinations of the density and viscosity of this alcohol that it was equally as pure and dry as that obtained by any of the other workers who used aluminium amalgam as a dehydrating agent.

Owing to the rapidity with which viscosity determinations could be carried out it was decided early in the course of the work to utilise this property as a routine method for testing the dryness of samples of alcohol. Table I shows the effect of increasing water content on the time of flow.

Table I.

Viscometer No. 2. Pipette A. Temperature 18°.

Water added %.	Time of flow (secs.).	Increase.
0·0	220·8	—
0·14	222·0	1·2
0·18	222·2	1·4
0·29	223·2	2·4
0·645	225·8	5·0
0·93	228·0	7·2
0·99	228·4	7·6
1·47	232·8	12·0

Table II.

Acetone added %.	Time of flow (secs.).	Decrease.
0·0	220·8	—
0·1	220·6	0·2
0·18	220·4	0·4
0·4	220·2	0·6
1·25	218·4	2·4

Table II gives similar figures for the addition of acetone. In the early stages of the work it was necessary to consider its presence, but later the alcohol supplied did not contain a detectable amount of this impurity.

The presence of water therefore increases the viscosity, whereas acetone has the opposite effect. One could be confident that similar results would be obtained at a higher temperature than 18° and when it was later decided to work at 25° the values were not redetermined since they had served their original purpose.

The Preparation of the Solutions.

Most of the salts used were Merck's "puriss." recrystallised. The specimens were heated at 150° until their weight was constant. Silica crucibles were used and the solutions made up in wide-necked Jena glass flasks.

With the weaker solutions, the addition of the methyl alcohol was carried out in a dry-box (Tutton, J., 1897, **71**, 865). Instead of drying the inside of the box with desiccating agents, as suggested by Tutton, a current of pure dry air was blown through the box for about an hour before any flasks were opened. The box was also fitted with suction apparatus for filling pyknometers.

Since the solution in no case approached saturation, no difficulty was experienced in dissolving the salts, the most obstinate, potassium chloride, passing into solution on standing with periodic shaking. In order to minimise the risk of introducing solid impurities, the solution after preparation was immediately transferred to a Jena flask with an externally ground stopper, further additions of alcohol being made to this when it was desired to dilute the solution. The greatest number of dilutions carried out with any one original solution was four.

The Determination of Density.

The densities were determined in two pyknometers which had a capacity of about 25 c.c. and were of the design described by Applebey (J., 1910, **97**, 2000) and by Hartley and Barrett (J., 1911, **99**, 1072). Two caps were used, one having a capillary head for use when filling the instrument and when it was suspended in the bath, and one closed for use when weighing. The use of the closed cap on the balance lessened the possibility of loss of solvent through evaporation by closing one of the openings to the air.

The filling of the pyknometer with alcohol or a solution was always carried out in the dry-box, since it was found by experiment that filling in the air with an ordinary water-pump introduced sufficient water seriously to affect the density. When the filling was effected

in the dry-box, the only likely error was that due to possible evaporation of part of the solvent. Since, however, the filling was a rapid process, taking not more than 3 minutes or so at the most, the loss of solvent would be small, and this was confirmed by the excellent agreement obtained when the density of the same solution was determined in two pyknometers of slightly different capacities and times of filling.

The determinations were carried out in a thermostat at 25°. The bath was electrically regulated, and the temperature, which was constant to 0·01°, was determined by reference to a thermometer standardised by the Reichsanstalt.

The weights used were standardised by Richards's method (*J. Amer. Chem. Soc.*, 1900, **22**, 144).

The formula used in the calculation of density was a reduced form of that recommended by Hartley and Barrett (*loc. cit.*), *viz.*,

$$\delta_l = \delta_w\{w_3 - (w_p - w_c)\}/\{w_2 - (w_p - w_c)\}.$$

δ_l = density of the liquid at the temperature of the determination referred to that of water at 4°.

δ_w = density of water at the temperature of the determination.

w_2 = apparent weight in air of the pyknometer when filled with water (corrected for air displaced by weights).

w_3 = apparent weight in air of the pyknometer when filled with the liquid (corrected for air displaced by weights).

w_p = true weight of the empty pyknometer in a vacuum.

w_c = true weight of the counterpoise in a vacuum.

This formula only requires the determination of w_3, since the correction for the change in density of air is beyond the limits of accuracy of this work (compare Barr, J., 1924, **125**, 1042).

The Determination of Viscosity.

The viscometers, of the U-shaped Ostwald type, were held in the thermostat in an apparatus designed to ensure that they always occupied the same relative position in the bath, and were adjusted to the vertical by means of a plumb-line. The openings to the air were guarded by soda-lime tubes so that the liquid came into contact with dry air only. The water values were frequently redetermined and were found not to change; when the instruments were not in use they were kept filled with conductivity water.

Filling was carried out by means of a 5 c.c. pipette, a method found satisfactory by Applebey (*loc. cit.*) and by Washburn and Williams (*J. Amer. Chem. Soc.*, 1913, **35**, 737). The filled viscometer was left in the bath for at least 10 minutes before any times were taken, the liquid being sent through the capillary at least twice in order to

wet the sides. The usual number of times of flow taken was seven. If any time varied by more than one-fifth of a second from the mean, the readings were abandoned and the viscometer was cleaned. This was seldom necessary.

The viscosity values were calculated from the formula

$$\eta_l = \eta_w \delta_l t_l / \delta_w t_w$$

η_l = viscosity of the liquid at the temperature of the determination.
η_w = viscosity of water at the temperature of the determination.
δ_l, δ_w = densities of the liquid and of water, respectively, at the temperature of the determination, referred to that of water at 4°.
t_l, t_w = observed times of flow of the liquid and of water respectively, in the same viscometer.

No correction for loss of kinetic energy was applied and no allowance was made for the air-column (Merton, J., 1910, **97**, 2454; Gruneisen, *Wiss. Abhandl. Physikal.-Tech. Reichsanst.*, 1905, **4**, 151; Applebey, *loc. cit.*). The value of $\delta_4^{25°}$ for water was taken as 0·997071, and that of the viscosity at 25° as 0·00895 (Goodwin and Mailey, *Physical Rev.*, 1908, **26**, 47).

The results obtained are set forth in the tables below, Table III containing the values for the density and viscosity of pure methyl alcohol, Table IV giving the values obtained for the solutions investigated, and Tables V and VI the viscosity increments and changes of volume on solution.

Densities are referred to water at 4° and viscosities are in absolute units. Concentrations are expressed in g.-mols. of salt per 1000 g. of solution.

TABLE III.

Density and viscosity of pure methyl alcohol at 25°.

Density.		Viscosity.	
Pyk. 1.	Pyk. 2.	Visc. 3.	Visc. 4.
0·78640	0·78641	0·005442	0·005456
	0·786405		
	0·78641		
Mean = 0·78641.		Mean = 0·00545.	

The density figures are each the mean of several adjustments of different fillings with different samples of alcohol. The density value interpolated from those given in Landolt and Bornstein's tables is 0·7866.

Dunstan (*loc. cit.*) gives the viscosity as 0·00546 and the value interpolated from the work of Thorpe and Rodger (*loc. cit.*) is 0·00553.

TABLE IV.

Densities and Viscosities of Solutions at 25°.

Salt.	Conc.	Density.	Viscosity. Visc. *a*.	Visc. *b*.	Mean.
KI	0·4951	0·84660	0·00662	0·00670	0·00667
	0·2577	0·81701	0·00608	0·00610	0·00609
	0·1930	0·81018	0·00594	0·00595	0·005945
	0·1643	0·80601	0·00587	0·00590	0·00588
	0·0916	0·79830	0·00571	—	0·00571
	0·08116	0·79597	0·00568	0·00570	0·00569
KBr	0·10884	0·79650	0·00575	0·00577	0·00576
	0·09926	0·794895	0·00573	0·00575	0·00574
	0·07192	0·79343	0·00566	0·00568	0·00567
	0·04446	0·79027	0·00560	0·00561	0·00560
	0·02840	0·78991	0·00553	0·00555	0·00554
KCl	0·04713	0·79150	0·00565	0·00565	0·00565
NaI	0·2753	0·81811	0·00628	0·00630	0·00629
	0·1306	0·80198	0·00586	0·00589	0·005875
	0·08303	0·79664	0·00572	0·00574	0·00573
	0·03870	0·79195	—	—	—
NaBr	0·6142	0·835624	0·00744	0·00745	0·007445
	0·3185	0·81169	0·00650	0·00651	0·006505
	0·15895	0·80027	0·00600	0·00602	0·00601

These results, when plotted, display no irregularities.

The values given by Tower (*loc. cit.*) for potassium iodide seem to agree with ours, but it is not possible to make a complete comparison, since he does not give the densities of his solutions, nor does it appear certain that his solvent was dry.

The viscosity increment is given by K/c, where c is the concentration and $K = (\eta_{\text{soltn.}} - \eta_{\text{alc.}})/\eta_{\text{alc.}}$

TABLE V.

Viscosity Increments.

Conc.	K.	K/c.	Conc.	K.	K/c.
Potassium iodide.			*Potassium bromide.*		
0·4951	0·224	0·452	0·1088	0·05688	0·5226
0·1643	0·079	0·480	0·09926	0·05321	0·5361
0·1930	0·0899	0·466	0·04446	0·02752	0·619
0·0916	0·0477	0·521	0·07192	0·0404	0·5631
0·08116	0·044	0·543	0·02840	0·01651	0·5813
Sodium bromide.			*Sodium iodide.*		
0·6142	0·367	0·598	0·2753	0·1541	0·5598
0·3185	0·1936	0·607	0·1306	0·0789	0·6042
0·15895	0·1028	0·646	0·08303	0·0514	0·622

The volume change on solution (V) is calculated by the method adopted by Hartley and Barrett (J., 1923, **123**, 398).

The figures for sodium iodide are omitted, since they display considerable discrepancies.

TABLE VI.

Conc.	Density.	*V.*	Conc.	Density.	*V.*
Potassium iodide.			*Potassium bromide.*		
0·4951	0·84460	27·6	0·10884	0·79650	41
0·2577	0·81701	28·4	0·09926	0·794895	31
0·1930	0·81018	27·5	0·07192	0·79343	49·5
0·1643	0·80601	30·0	0·04446	0·79027	34
0·0916	0·79830	28·3	0·02840	0·78991	56
0·08116	0·79597	28·4			
			Sodium bromide.		
			0·6142	0·835624	26·1
			0·3185	0·81169	26·8
			0·15895	0·80027	42·0

In conclusion, the authors wish to express their thanks to the Chemical Society for a grant which defrayed part of the cost and to Brig.-Gen. H. Hartley and Mr. W. H. Barrett for the interest they have taken in the work.

EXETER COLLEGE, OXFORD. [*Received, May 20th*, 1926.]

CCLIII.—*Constitution of the Yellow Sodium Compounds formed from Ethyl Citraconate (or Itaconate) and Ethyl Sodiomalonate.*

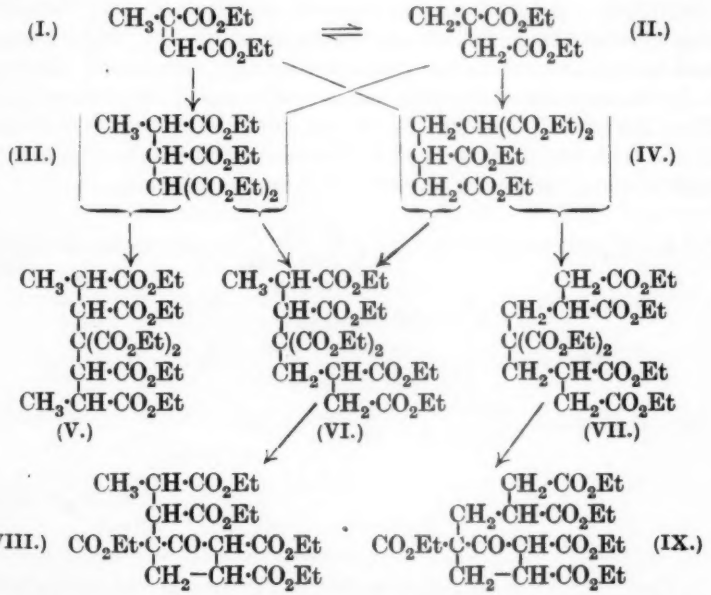
By CHRISTOPHER KELK INGOLD and CHARLES WILLIAM SHOPPEE.

THE action of ethyl sodiomalonate on ethyl citraconate has been examined by Michael (*Ber.*, 1900, **33**, 3757), by Hope (J., 1912, **101**, 892), and by Ingold, Shoppee, and Thorpe (this vol., p. 1477). The combined results of these investigations show that, in alcoholic solution under the conditions of the condensation, ethyl citraconate (I) and ethyl itaconate (II) are directly interconvertible, so that whichever is used as the initial substance, products are obtained which are derived from both. It has also been proved that the primary addition product of ethyl malonate to ethyl citraconate has constitution (III), and the primary addition product to ethyl itaconate has constitution (IV).

Owing principally to the reactivity of the addition products (III) and (IV), the whole reaction is actually much more complex than the above simple statement indicates, and amongst the by-products described by Ingold, Shoppee, and Thorpe was an insoluble, remarkably stable, yellow sodio-derivative, the constitution of which was left undetermined. This substance has now been investigated, and the elucidation of its structure forms the subject of the present communication.

Actually, the sodium "compound" is a difficultly separable mixture of two closely similar isomerides. On acidification, the corresponding ketonic esters are obtained. One is a liquid characterised by an acid, m. p. 149°, which it yields on hydrolysis. The second, present in greater quantity, is a solid, m. p. 83°; on hydrolysis, it gives an acid, m. p. 173°.

Analysis shows that these two ketonic esters are derived by the elimination of alcohol from one or more of the products of the further addition to ethyl citraconate or ethyl itaconate (I, II) of either of the primary addition products (III or IV), both of which are mono-substituted malonic esters. If it may be assumed that these substituted malonic esters would add to citraconic and itaconic esters in the same directions as have been established for the addition of malonic ester itself, then it follows that the three possible addition compounds must have the structures (V), (VI), and (VII). Now these three esters might conceivably lose alcohol in a large number of ways, giving a variety of derivatives of *cyclo*pentanone and *cyclo*hexanone; there are, nevertheless, only two structurally isomeric formulæ (VIII and IX) which are consistent with the properties of the ketonic esters obtained.



Both these esters give a colour with ferric chloride and form insoluble yellow sodio-compounds; they must, therefore, each contain the grouping ·CO·CH·CO_2Et. This might arise in a Dieckmann

reaction by the elimination of alcohol either from $CO(OEt) + (H)CH{\cdot}CO_2Et$, or from $CO_2Et{\cdot}CH{\cdot}CO(OEt) + (H)C{\cdot}CO_2Et$. The second alternative is, however, excluded in the present case, since the group $\cdot CH(CO_2Et)_2$ is not contained in any of the esters (V), (VI), (VII). The loss of alcohol must therefore take place from $CO_2Et + CH_2{\cdot}CO_2Et$, and this at once removes formula (V) from consideration, since it does not contain the group $-CH_2{\cdot}CO_2Et$.

Both ketonic esters, on hydrolysis by mineral acids, evolve two molecules of carbon dioxide along with five of ethyl alcohol, two carbethoxyl groups being thus completely eliminated in each case. This is taken to show the presence of the system $CO_2Et{\cdot}C{\cdot}CO{\cdot}C{\cdot}CO_2Et$, which can only be formed from $\cdot CO_2Et + \cdot CH_2{\cdot}CO_2Et$ (preceding paragraph) if the carbethoxyl group concerned in the elimination of alcohol is itself part of the system $CO_2Et{\cdot}C{\cdot}CO_2Et$. In this case, ring closure must take place between the groups $\cdot CH_2{\cdot}CO_2Et$ and $>C(CO_2Et)_2$ in (VI) and (VII), the cyclic products having the structures (VIII) and (IX) respectively.

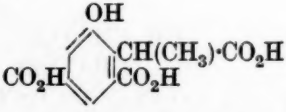
There is one remaining possibility, namely, that the loss of two carbethoxyl groups on hydrolysis arises from the independent occurrence in the molecule of the groups $\cdot CO{\cdot}CH{\cdot}CO_2Et$ and $>C(CO_2Et)_2$. *cyclo*Butane, *cyclo*heptane, and *cyclo*octane structures being ignored, there is only one formula containing these groups which is consistent with the properties already mentioned, namely, the *cyclo*hexane structure (X), which might conceivably arise from (VI). We exclude it, however, on the grounds that neither of the tribasic acids obtained by acid hydrolysis of the two ketonic esters could be converted into a phenolic acid by bromination:

$$(\text{VI.}) \rightarrow CH_3{\cdot}CH(CO_2Et){\cdot}CH\begin{matrix}<CO{\cdot}CH(CO_2Et)\\ C(CO_2Et)_2{\cdot}CH_2\end{matrix}>CH{\cdot}CO_2Et \quad (\text{X.}) \xrightarrow[\text{lysis})]{\text{(Hydro-}}$$

$$CH_3{\cdot}CH(CO_2H){\cdot}CH\begin{matrix}<CO\text{———}CH_2\\ CH(CO_2H){\cdot}CH_2\end{matrix}>CH{\cdot}CO_2H \xrightarrow{(2Br_2)}$$

$$CH_3{\cdot}CH(CO_2H){\cdot}CBr\begin{matrix}<CO\text{———}CHBr\\ CH(CO_2H){\cdot}CH_2\end{matrix}>CH{\cdot}CO_2H \xrightarrow{(-2HBr)}$$

$$CH_3{\cdot}CH(CO_2H){\cdot}C\begin{matrix}<CO\text{———}CH\\ C(CO_2H){\cdot}CH_2\end{matrix}>C{\cdot}CO_2H =$$



It does not, of course, follow immediately that, of the two ketonic esters isolated, one has formula (VIII) and the other formula (IX), since each of these obviously represents several possible stereoisomeric forms, including, in each case, forms which could give different

tribasic acids on hydrolysis. There remain, therefore, three alternatives: either the two ketonic esters are stereoisomeric modifications of (VIII) (hypothesis *a*), or they are stereoisomeric forms of (IX) (hypothesis *b*), or one is a form of (VIII) and the other is a form of (IX) (hypothesis *c*).

Now, according to the scheme on p. 1913, the condensation of the pure ester (III) with either citraconic or itaconic ester (experiment A) should yield forms of (VIII) only, whereas the condensation of the isomeric ester (IV) with either ethyl citraconate or ethyl itaconate (experiment B) might give modifications of both (VIII) and (IX). Hence, according to hypothesis (*a*), experiment A should yield the two known ketonic esters, whilst experiment B should give not only these but also new isomerides. According to hypothesis (*b*), experiment A could only yield new isomerides, whilst experiment B would be expected to give the known substances. Finally, according to hypothesis *c*, experiment A should give one of the known isomerides only (that which has formula VIII), whilst experiment B should yield a mixture of both, similar to the mixture formed in the original condensations of citraconic and itaconic esters with malonic ester.

Actually the observations accorded with hypothesis *c*, experiment A yielding only the liquid ester corresponding with the tribasic acid, m. p. 149°. Experiment B gave a mixture of the same liquid ketonic ester and the solid isomeride, m. p. 83°, the latter being formed in larger proportion as in the original condensation. Hence the liquid ester has formula (VIII) and the solid one formula (IX).

It follows that the original insoluble yellow sodio-derivative is a mixture of (XI) and (XII) containing an excess of (XII), and that the tribasic acids, m. p.'s 149° and 173°, have formulæ (XIII) and (XIV) respectively.

(XI.) $CO_2Et\cdot C{:}C(ONa)\cdot C(CO_2Et)\cdot CH\cdot CO_2Et$
$CO_2Et\cdot CH\text{———}CH_2 \qquad CHMe\cdot CO_2Et$

(XII.) $CO_2Et\cdot C{:}C(ONa)\cdot C(CO_2Et)\cdot CH_2\cdot CH\cdot CO_2Et$
$CO_2Et\cdot CH\text{———}CH_2 \qquad CH_2\cdot CO_2Et$

$CH_2\cdot CO\cdot CH\cdot CH(CO_2H)\cdot CHMe \qquad CH_2\cdot CO\cdot CH\cdot CH_2\cdot CH\cdot CO_2H$
$CO_2H\cdot CH\text{——}CH_2 \qquad CO_2H\ CO_2H\cdot CH\text{——}CH_2 \qquad CH_2\cdot CO_2H$
(XIII.) (XIV.)

On oxidation with permanganate, the acid (XIV) yields an acid $C_{10}H_{14}O_8$, which appears to be the glutaric acid,

$CO_2H\cdot CH_2\cdot CH_2\cdot CH(CO_2H)\cdot CH_2\cdot CH(CO_2H)\cdot CH_2\cdot CO_2H$

(XV), to be expected from the oxidative fission of a *cyclo*pentanone.

EXPERIMENTAL.

The various methods of condensing ethyl sodiomalonate with ethyl citraconate have been described by Ingold, Shoppee, and Thorpe (*loc. cit.*). In order to obtain the sodium compounds, the product from 105 g. of ethyl citraconate, 91 g. of ethyl malonate, and 26 g. of sodium in 300 g. of alcohol was poured into water. After vigorous shaking to coagulate the precipitate, this was collected, washed with a little alcohol and with water, and dried. The best yields (10 g.) were obtained when the original mixture was heated on the steam-bath for at least 4 hours before being worked up. The mixture of sodium compounds is sparingly soluble in alcohol and the alcoholic solution gives a bright crimson colour with ferric chloride.

Ethyl ω-1 : 3 : 4-*Tricarbethoxy*-2-*keto*-cyclo*pentylmethylsuccinate* (IX).—(*a*) The mixed sodio-derivatives (30 g.) were shaken with hydrochloric acid and ether until no solid remained. The nearly colourless oil obtained from the ethereal layer (dried with sodium sulphate) soon crystallised and then separated from ether–ligroin or alcohol in colourless needles, m. p. 83° (Found: C, 56·7; H, 6·8. $C_{23}H_{34}O_{11}$ requires C, 56·7; H, 7·0%). The ester gives a cherry-red colour with aqueous alcoholic ferric chloride.

(*b*) Ethyl citraconate (4 g.) and ethyl butane-αββδ-tetracarboxylate (7 g.) were heated together for 3 hours in presence of alcoholic sodium ethoxide (sodium, 1 g.; ethyl alcohol, 12 g.). The paste of crystals obtained was mixed with water, and the solid collected, from which the esters were regenerated, and the isomeride, m. p. 83°, separated, as in the preceding experiment.

ω-4-*Carboxy*-2-*keto*cyclo*pentylmethylsuccinic Acid* (XIV).—The above ester was heated for 1 hour on the steam-bath with 30% hydrochloric acid under a condenser short enough to permit the escape of alcohol vapour. The solution so obtained was evaporated in an open basin on the steam-bath, and the solid residue crystallised from hydrochloric acid; tufts of needles were then obtained, m. p. 173° (yield, 85%) (Found: C, 51·1; H, 5·5; *M*, by titration, 257. $C_{11}H_{14}O_7$ requires C, 51·1; H, 5·5%; *M*, 258).

Ethyl α-1 : 3 : 4-*Tricarbethoxy*-2-*keto*-cyclo*pentyl*-β-*methylsuccinate* (VIII).—(*c*) Ethyl citraconate (4 g.), ethyl butane-ααβγ-tetracarboxylate (7 g.), and alcoholic sodium ethoxide (sodium, 1 g.; ethyl alcohol, 12 g.) were heated on the steam-bath for 3 hours, and the flocculent product obtained on dilution with water was treated with hydrochloric acid and ether. The oil thus obtained (Found: C, 56·4; H, 6·7. $C_{23}H_{34}O_{11}$ requires C, 56·7; H, 7·0%) gave a bright red colour with ferric chloride. The ester was characterised by conversion into the tribasic acid described below.

(*d*) The same substance may be obtained from the oily by-product accompanying the ester of m. p. 83° in experiments (*a*) and (*b*) above.

α-4-*Carboxy*-2-*keto*cyclo*pentyl*-β-*methylsuccinic Acid* (XIII).—The ester (VIII) was hydrolysed with hydrochloric acid as in the preparation of the isomeric acid (XIV). The acid so obtained crystallised from acetone–benzene in needles, m. p. 148—149° (Found: C, 51·1; H, 5·8. $C_{11}H_{14}O_7$ requires C, 51·1; H, 5·5%).

Ethyl ω-4-*Carbethoxy*-2-*keto*cyclo*pentylmethylsuccinate*, prepared by esterification of the acid (XIV) with alcoholic sulphuric acid in the usual manner, had b. p. 247°/18 mm. and gave no colour with ferric chloride (Found: C, 59·6; H, 7·5. $C_{17}H_{26}O_7$ requires C, 59·6; H, 7·6%).

The *semicarbazone*, obtained from the ester and semicarbazide acetate in cold aqueous alcoholic solution, had m. p. 105° after crystallisation from dilute alcohol (Found: C, 54·1; H, 7·4. $C_{18}H_{29}O_7N_3$ requires C, 54·1; H, 7·3%).

βδ-*Dicarboxysuberic Acid* (XV).—A solution of the acid (XIV) (2 g.) in aqueous sodium hydrogen carbonate was treated with 3% potassium permanganate in the cold. The reaction, slow initially, accelerated, and then became slow again when 29 c.c. had been added. A further 29 × 2·2 c.c. were then added rapidly, and the mixture was kept over-night. After treatment of the manganese oxides with steam, the combined filtrates were evaporated to small bulk, and the liquid was made acid with hydrochloric acid, boiled, and rendered alkaline with ammonia; addition of calcium chloride then gave calcium oxalate. The filtrate was strongly acidified and extracted with ether. On concentration of the dried ethereal solution, a crystalline acid was obtained, but complete evaporation yielded a gum which frothed and filled the desiccator when the attempt was made to pump off the last traces of ether. The solid acid had m. p. 206—207° and was stable to permanganate (Found: C, 45·7; H, 4·8. $C_{10}H_{14}O_8$ requires C, 45·8; H, 5·3%).

The ethyl butane-ααβγ-tetracarboxylate and ethyl butane-αβδδ-tetracarboxylate used in these experiments were characterised through their amides, of which *butane-ααβγ-tetracarboxyamide* is a new compound. It is readily obtained from the ester and aqueous ammonia, and, after crystallisation from boiling water, has m. p. 267° (decomp.) (Found: C, 41·8; H, 6·3. $C_8H_{14}O_4N_4$ requires C, 41·7; H, 6·1%).

We desire to thank the Royal Society for a grant with the aid of which the expenses involved in this work have been met.

THE UNIVERSITY, LEEDS. [*Received, June 1st,* 1926.]

CCLIV.—*The Isomerism of the Oximes. Part XXV. The Dissociation Constants of some Isomeric Aldoximes.*

By Oscar L. Brady and Richard F. Goldstein.

Although no measurements of dissociation constants of aldoximes have been recorded in the literature, it has been shown qualitatively by two methods that the aromatic α-aldoximes are stronger acids than the corresponding β-aldoximes. From approximate cryoscopic measurements, Goldschmidt and Röder (*Ber.*, 1895, **28**, 2013) concluded that in aqueous solution the sodium salts of the α-aldoximes are mainly electrolytically dissociated, whilst the sodium salts of the β-aldoximes are mainly hydrolytically dissociated. Later, Swientoslawski and his co-workers (Swientoslawski, *Chem. Polski*, 1918, **15**, 1; Swientoslawski and Papow, *ibid.*, 1919, **16**, 1; Dorobialska, *Rocz. Chem.*, 1921, **1**, 424), by thermochemical measurements of the heats of neutralisation of the aldoximes with sodium hydroxide, found that the sodium salts of the β-aldoximes were hydrolysed to a somewhat greater extent than the corresponding α-compounds. His method, however, gave but approximate results, and as he worked on only two aldoximes (benzaldoxime and *m*-nitrobenzaldoxime), his results require confirmation.

An investigation of the dissociation constants of some isomeric aldoximes has been undertaken in the hope that it might throw some light upon the isomerism of the oximes. The aldoximes are weak acids, analogous to phenol, and hence their dissociation constants can be determined only hydrolytically. Of the methods available, that depending on the measurement of the degree of hydrolysis of the sodium salt by conductivity methods was finally chosen as the most suitable (Lundén, Ahrens' Sammlung, 1908, **14**, 42), and the dissociation constants of the aldoximes recorded in the table on p. 1923 have been determined.

It was unfortunately impossible to determine the dissociation constants of more than five β-aldoximes, on account of their very sparing solubility; even with those which were sufficiently soluble, conductivity measurements could be taken only at two dilutions, and were greatly hampered by decomposition caused by the platinum black on the electrodes.

From the values of the four pairs of isomeric aldoximes which were investigated, it will be seen that in all cases the α-aldoxime possesses a higher dissociation constant than the β-aldoxime, thereby confirming the conclusions of Goldschmidt and Röder and of Swientoslawski and his co-workers.

It was hoped that this research might give some clue to the reasons for the formation or non-formation of two forms of substituted benzaldoximes; it has been shown (Brady and Dunn, J., 1923, **123**, 1783) that the conversion of the α- into the β-isomeride through the hydrochloride depends upon an isomeric change in the hydrochloride itself and it was thought that the acidity of the oxime might have some bearing on the stability of the ammonium-type hydrochloride which, it was considered, was formed in the first instance; these expectations have not been realised. For example, although all attempts to obtain the β- form from α-*o*-methoxybenzaldoxime have been unsuccessful, whilst α-*p*-methoxybenzaldoxime is very easily converted into the β-compound, yet the two α-oximes have practically the same dissociation constants ($1{\cdot}3 \times 10^{-11}$ and $1{\cdot}2 \times 10^{-11}$, respectively). Again, the α-oxime-forming hydrochlorides of benzaldoxime and *p*-methoxybenzaldoxime change to the β-oxime-forming hydrochlorides at considerably lower temperatures than those of 3 : 4-dimethoxybenzaldoxime and 3 : 4-methylenedioxybenzaldoxime. There seems, however, to be a tendency for the α-oxime-forming hydrochlorides of the more strongly acidic oximes to be the least stable; roughly, the α-oxime-forming hydrochlorides can be arranged in order of their relative stabilities as follows, the values of their dissociation constants being shown in brackets: 3 : 4-methylenedioxybenzaldoxime ($1{\cdot}4 \times 10^{-11}$) > *p*-methoxybenzaldoxime ($1{\cdot}2 \times 10^{-11}$) > benzaldoxime ($2{\cdot}1 \times 10^{-11}$) > *m*-nitrobenzaldoxime ($7{\cdot}0 \times 10^{-11}$) > *p*-nitrobenzaldoxime ($10{\cdot}7 \times 10^{-11}$).

The isomeric change may therefore be the rearrangement of the molecule to the form which most favours hydrochloride formation, that is, the least acidic.

Doubt has recently been cast upon Hantzsch's original formulation of the configuration of the aldoximes (*Ber.*, 1891, **24**, 13), and it has been suggested that the α-isomeride has the so-called *syn*- and not the *anti*-configuration assigned to it by him.

Apart from the chemical evidence in favour of this suggestion (Brady and Bishop, J., 1925, **127**, 1357; Auwers and Ottens, *Ber.*, 1925, **58**, 2060; Meisenheimer, Zimmermann, and Kummer, *Annalen*, 1926, **446**, 205), some evidence has been adduced from a consideration of the physical properties.

Beckmann, Liesche, and Correns (*Ber.*, 1923, **56**, 341) have suggested configurations for the aldoximes, based upon Abegg's electrochemical theory of the stability of the oximes (*Ber.*, 1899, **32**, 291); to quote from their paper "the higher-melting aldoximes, which readily form nitriles, are favoured by the action of acids, and must be represented as (I); the isomerides, which can be

acylated and hydrolysed without decomposition, must then be represented as (II) :

Apart from the question of the validity of Abegg's electrochemical theory, the facts from which these deductions are drawn are incorrect. In accepting Abegg's theory, Beckmann, Liesche, and Correns acquiesced in his statement that the α-aldoximes are stable to alkali, and the β-aldoximes stable to acid; but this is not so, since the β-aldoximes of the aromatic series and their *O*-ethers are more or less rapidly converted into the corresponding α-compounds by the action of a small amount of acid (compare, *inter alia*, Luxmoore, J., 1896, **69**, 179; Brady and Dunn, J., 1923, **123**, 1788), whilst when dissolved in alkali, they are comparatively stable (compare Brady, J., 1914, **105**, 2114). The facts are that at low temperatures the α-oxime-forming hydrochloride, and at higher temperatures the β-oxime-forming hydrochloride, is stable, the temperature of transition varying with the individual oxime.

Auwers and Ottens (*Ber.*, **1924**, **57**, 446) consider that their measurements of the optical properties of the aldoximes and the *O*-ethers favour the new formulation, but it is doubtful if these properties are a trustworthy guide when small differences of constitution are involved (compare Goss, Ingold, and Thorpe, J., 1924, **125**, 1927). On the other hand, if the principle, applied by Ostwald (*Z. physikal. Chem.*, 1892, **9**, 553) to the acids of the ethylene series, that in an acid the proximity of a so-called " acidic " group tends to increase the dissociation constant of the acid, can be applied to the aldoximes, the benzaldoxime of the *anti*-type, where the negative phenyl group is vicinal to the aldoximino-hydroxyl group, should have a higher dissociation constant than the *syn*-isomeride, in which the two groups are farther apart.

It has been possible to determine the dissociation constants of four pairs of isomeric aldoximes (see table on p. 1923) and in all these cases the α-aldoxime has a higher dissociation constant than the β-isomeride. A configuration of the *anti*-type should therefore be assigned to the α-aldoximes, and of the *syn*-type to the β-aldoximes, supporting Hantzsch's original view of the configuration of the aldoximes.

In all cases of isomerism in the ethylenic series, the *cis*-form has a greater solubility in water than the *trans*-form (Michael, *J. Amer. Chem. Soc.*, 1918, **40**, 1678). Since an *anti*-aldoxime corresponds to the *cis*-form, and a *syn*-aldoxime to the *trans*-form (Auwers and

Ottens, *Ber.*, 1924, **57**, 446),* one would expect the former to be more soluble in water than the latter. Although no quantitative data on the solubility of the aldoximes have been published, it is well known that the α-aldoxime is more soluble in water (and in most other solvents) than the β-aldoxime. The conclusions to be drawn from these considerations therefore agree with those drawn from measurements of dissociation constants.

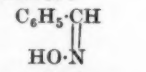
The deductions from the physical properties of the aldoximes are thus at variance with those drawn from their chemical reactions, and it must be admitted that we are far from achieving finality.

It had been hoped, when this work was commenced, to follow the inversion of the β- to the α-aldoxime by measuring the change of conductivity with time of a solution of the sodium salt of a β-aldoxime, but unfortunately the β-aldoxime appears to suffer a profound decomposition in contact with the platinum-black used on the electrodes, and the curve obtained was inexplicable. Also attempts to detect any transient basic or acidic properties of an aldoxime on liberation from its sodium salt were unsuccessful. One other point deserves mention : it was found that on heating *o*-nitrobenzaldoxime with dilute sodium hydroxide, *o*-nitrobenzamide was produced in fair yield. It was at first thought that this was due to a Beckmann rearrangement, but Reissert (*Ber.*, 1908, **41**, 3815) has found that on heating α-*o*-nitrobenzaldoxime with a very weak alkali, such as potassium cyanide, an excellent yield of *o*-nitrobenzonitrile was produced, but that on increasing the strength of the alkali, *o*-nitrobenzamide, mixed with a little *o*-nitrobenzonitrile, was formed. The reaction appears to be an interesting case of dehydration followed by addition of water in a different direction, and is unique for *o*-nitrobenzaldoxime; with other oximes, either there is no change (α-3 : 4-methylenedioxybenzaldoxime, α-*p*-methoxybenzaldoxime), or complete decomposition takes place (α-6-nitro-3 : 4-methylenedioxybenzaldoxime).

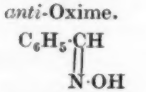
Experimental.

The method used was that first devised by Walker (*Z. physikal. Chem.*, 1889, **4**, 319) and subsequently developed and improved by Bredig (*ibid.*, 1894, **13**, 289).

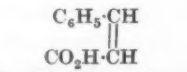
* The correspondence can be seen by comparing the cinnamic acids with the benzaldoximes :



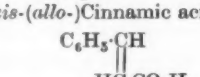
anti-Oxime.



syn-Oxime.



cis-(*allo*-)Cinnamic acid.



trans-Cinnamic acid.

If the observed conductivity of a solution of one mol. of the sodium salt of an oxime dissolved in v litres ofwater is $\Lambda_{obs.}$, the true conductivity of the unhydrolysed salt Λ_v, and the conductivity of the sodium hydroxide formed by hydrolysis Λ_{NaOH}, then the degree of hydrolysis, x, can be obtained from the equation :

$$\Lambda_{obs.} = (1 - x)\Lambda_v + x\Lambda_{NaOH}.$$

Furthermore, the hydrolysis constant, K_h, of the sodium salt is given by :

$$K_h = x^2/v(1 - x).$$

Finally,

$$K_a = K_w /K_h,$$

where K_a is the dissociation constant of the oxime, and K_w is the ionisation constant of water, assumed to be $1{\cdot}0 \times 10^{-14}$ as the mean of the most trustworthy determinations. By means of these three equations, K_a can be calculated from measurements of $\Lambda_{obs.}$, Λ_v and Λ_{NaOH}. Owing to experimental difficulties, Λ_v could not be directly measured, and had to be assumed from the empirical rules of Ostwald (" Lehrbuch der Allgemeine Chemie," II, i, p. 619) and Bredig (*loc. cit.*, p. 198).

The preparation of the oxime calls for no special remark. The crude oxime was recrystallised from suitable solvents, generally benzene and light petroleum, or dilute alcohol, until the m. p. recorded in the literature was obtained. A solution of the sodium salt was prepared by dissolving a weighed amount of the oxime in the calculated quantity of carbon dioxide-free sodium hydroxide and diluting the solution to the required volume. The sodium hydroxide was made by the action of water vapour on metallic sodium suspended on nickel gauze under a bell-jar through which was passed a slow current of carbon dioxide-free air to remove the hydrogen as it was formed ; omission of this precaution led to several explosions. The strength of the sodium hydroxide was determined by titration against pure succinic acid. Solutions were preserved in silica vessels.

The conductivity measurements were made at $25° \pm 0{\cdot}02°$, with a rotating double commutator, a Wheatstone bridge, and suspended-coil galvanometer. The bridge-wire was calibrated by the method recommended by Kohlrausch (" Leitvermögen der Elektrolyte," 1916, p. 48) and the resistances were checked against a standard resistance. An enclosed cell of hard glass was used for the alkaline solutions. The conductivity of the sodium hydroxide in the same dilutions as were used was frequently determined, and the values obtained were employed in the calculations. In all measurements, carbon dioxide-free water of conductivity $1{\cdot}5 - 2{\cdot}0 \times 10^{-6}$ mho

was employed and the readings were corrected for this value. Determinations were made at as many as possible of the usual dilutions 32, 64, 128, 256, 512, and 1024 (see col. 3 in table).

Considerable difficulty was experienced with the β-oximes, as freshly deposited platinum black decomposed the sodium salts, bringing about a rapid fall of conductivity. This effect appears to be quite general for all β-aldoximes, *e.g.*, the sodium salt of β-heptaldoxime, which is only known in one form, is rapidly decomposed. It was ultimately found possible to destroy the activity of the electrodes, without impairing the accuracy of the conductivity measurements, by leaving them in contact with the sodium salt of a β-aldoxime for some time. By this means, the required conductivities could be determined satisfactorily.

TABLE.

Oxime.	M. p.	*v* (litres).	$K_h \times 10^5$. Limits.	Mean	$K_a \times 10^{11}$.
α-Benzaldoxime	35°	32—1024	42—51	47	2·1
β- ,, ...	131—132	512—1024	210—220	215	0·47
α-*o*-Nitro-benzaldoxime ...	101—102	32—1024	10·6—12·2	11·5	8·7
β-*o*-Nitro- ,, ...	143—145	512—1024	54—56	55	1·8
α-*m*-Nitro- ,, ...	121	32—1024	13·7—14·8	14·3	7·0
β-*m*-Nitro- ,, ...	119—120	512—1024	55—58	56	1·8
α-*p*-Nitro- ,, ...	129	32—1024	8·9—10·3	9·3	10·7
α-2 : 4-Dinitro- ,, ...	127	128—1024	3·3—2·3	2·7	37 *
α-*o*-Methoxy- ,, ...	92	32—1024	71—78	75	1·3
α-*m*-Methoxy- ,, ...	38—39	128—1024	36—40	39	2·6
α-*p*-Methoxy- ,, ...	65	256—1024	80—84	82	1·2
α-3 : 4-Dimethoxy- ,, ...	94	128—1024	69—76	73	1·4
α-3 : 4-Methylenedioxy- ,,	111—112	64—1024	71—76	74	1·4
α-Cinnamaldoxime	75—76	128—1024	35—37	36	2·8
β- ,, ...	135	512—1024	71—82	77	1·3
α-*m*-Nitrocinnamaldoxime	157	1024	14·5	14·5	6·9 †
β-Heptaldoxime	55—56	512—1024	380—410	395	0·25

* With α-2 : 4-dinitrobenzaldoxime, the hydrolysis constant decreased regularly on dilution from 128 to 1024 litres. This change is probably due to partial conversion of the oxime into 4-nitrosalicylonitrile (Borsche, *Annalen*, 1912, **390**, 1).

† No consistent results could be obtained with this oxime at a dilution of 2048 litres. The value at 1024 litres has been confirmed by repetition.

Action of Alkali on o-Nitrobenzaldoxime.—A mixture of the α-oxime (1·32 g.) with an equivalent weight of *N*/5-sodium hydroxide was heated on the water-bath for 3 hours, left over-night, and heated for another 2 hours. The solution contained about 0·03 g. of sodium nitrite (estimated by Griess's colorimetric method) and the issuing vapours contained ammonia. On cooling and saturating the solution with carbon dioxide, a nearly white precipitate (0·22 g.) was obtained. Nothing could be isolated from the solution after filtration, and no salicylic acid was present. The precipitate (m. p. 172—175°) was

shown to be *o*-nitrobenzamide by its reactions, and by a mixed m. p. with an authentic specimen.

About a 10% yield of *o*-nitrobenzamide can be obtained by boiling either the α- or the β-oxime for 15 minutes with double the equivalent quantity of *N*/5-sodium hydroxide. In this case, the amide separated on cooling, and treatment of the filtrate with carbon dioxide yielded an impure oxime.

Neutralisation Phenomenon with α-m-*Nitrobenzaldoxime.*—10 C.c. of *N*/128-hydrochloric acid were mixed with 10 c.c. of an *N*/128-solution of the sodium salt of α-*m*-nitrobenzaldoxime, and the conductivity was measured at frequent intervals, but no change was observed during 100 minutes, the equivalent conductivity being 126·4. The value given by Jones (Carnegie Inst. Pub., No. 170, 1912) for the equivalent conductivity of sodium chloride in *N*/256-solution is 124·1. It is therefore clear that no abnormal phenomenon takes place on neutralisation of the sodium salt of α-*m*-nitrobenzaldoxime.

In conclusion, one of us (R. F. G.) wishes to thank the Department of Scientific and Industrial Research for a maintenance grant which enabled him to take part in this work.

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CCLV.—*The Estimation of Ferro- and Ferri-cyanides.*

By WILLIAM MURDOCH CUMMING and WILLIAM GOOD.

BY making use of the fact that solutions of ferrocyanides precipitate, from a solution of benzidine dihydrochloride, a sparingly soluble white salt, $3C_{12}H_{12}N_2,H_4Fe(CN)_6,H_2O$, Cumming (J., 1924, **125**, 240) estimated gravimetrically and volumetrically the ferrocyanides of sodium, potassium, and calcium. Satisfactory results were obtained, but the use of hypobromite as an external indicator in the volumetric process required some practice. By altering the method of estimation, however, it is possible to replace it by phenolphthalein. Mr. R. Fleming, of The Cairo School of Medicine, has kindly informed us that benzidine gives a blue coloration with a mixture of copper sulphate and ammonium thiocyanate solutions. The coloration, however, is produced only under certain conditions of concentration.

The gravimetric method outlined in the previous paper has now been extended to other soluble and also to insoluble ferrocyanides,

and the volumetric method has been improved so as to render the end-point easy of detection. Both methods have also been applied to soluble ferricyanides, which give with benzidine dihydrochloride (Cumming, J., 1924, **125**, 1107) a sparingly soluble, bluish-violet precipitate, $3C_{12}H_{12}N_2,H_3Fe(CN)_6,3H_2O$ (Found: Fe, 6·8. Theory requires Fe, 6·8%).

Estimation of Ferrocyanides.—For soluble ferrocyanides, the gravimetric method (*G.M.*) is that already described, 0·2 g. of the salt being used. An insoluble ferrocyanide (0·5 g.) is dissolved in sodium hydroxide or decomposed by carbonate solution, and the metal removed by suitable means (see later). The filtrate is exactly neutralised with dilute hydrochloric acid, methyl-orange being used as indicator, and an excess of a saturated solution of benzidine dihydrochloride is added. The precipitate is filtered off, washed, dried, and ignited as before. By multiplying the weight of ferric oxide obtained by the factor given, the weight of anhydrous ferrocyanide is obtained.

The principle of the new volumetric method (*V.M.*) consists in adding to a neutral solution of the ferrocyanide a measured quantity (excess) of a standard solution of benzidine dihydrochloride. The precipitated benzidine hydroferrocyanide is filtered off, and the hydrochloric acid in the filtrate estimated with standard alkali and phenolphthalein. In the case of the insoluble ferrocyanides, the heavy metal is removed as in the gravimetric method, and the measured excess of the benzidine then added to the carefully neutralised filtrate.

The volumetric method depends on the reaction $3[B,2HCl] + M_4Fe(CN)_6 = 3B,H_4Fe(CN)_6 + 4MCl + 2HCl$. The hydrochloric acid produced is equivalent to one-third of that present in the benzidine dihydrochloride used in the reaction. Hence, if 1 c.c. of alkali solution is equivalent to b c.c. of benzidine dihydrochloride solution and n and x are the number of c.c. of benzidine dihydrochloride solution added, and used in the reaction, respectively, then the total alkali (c.c.) required after the reaction, $a = (n - x)/b + x/3b$, whence $x = 1{\cdot}5(n - ab)$. Hence, since the concentration of benzidine dihydrochloride is known, the amount of the original ferrocyanide can be calculated; or $x/3b$ represents the volume of standard alkali equivalent to the free hydrochloric acid produced, and this is proportional to the amount of ferrocyanide originally present.

Estimation of Ferricyanides.—The gravimetric method is similar to that used in the case of the ferrocyanides, but a large excess of benzidine dihydrochloride (250 c.c. of the saturated solution for 0·2 g. of ferricyanide) is required to complete the precipitation

of the benzidine hydroferricyanide. A test should be made, however, to ascertain if precipitation is complete.

The volumetric method is the same as for ferrocyanides, but again a large measured excess of benzidine dihydrochloride is required. The reaction is represented by $3[B,2HCl] + M_3Fe(CN)_6 = 3B,H_3Fe(CN)_6 + 3MCl + 3HCl$. The hydrochloric acid produced is equivalent to one-half of the quantity present in the benzidine dihydrochloride used in the reaction. In the same notation as before, $x = 2(n - ab)$. The quantity of ferricyanide can therefore be calculated; or, as before, the amount of ferricyanide $\propto$ HCl produced $\propto x/2b$ (c.c. of standard alkali).

Both the gravimetric and the volumetric method give accurate results, and are very easily carried out. Both methods may be applied to the same sample of the salt; the former estimation is obtained from the precipitate of the organic salt, the latter from the filtrate after removal of the organic salt.

Experimental.

Standard benzidine dihydrochloride solution is prepared by dissolving, with the aid of slight heat, about 3·5 g. of pure benzidine in a litre of water containing the calculated quantity of chlorine-free hydrochloric acid, or by dissolving about 4 g. of pure benzidine dihydrochloride in a litre of water. In the former case, if the benzidine is not quite pure, the solution should be standardised, gravimetrically, against a pure ferrocyanide. In the latter case, if the salt contains some monohydrochloride, as it often does when recrystallised from water (see Cumming, *J. Soc. Chem. Ind.*, 1923, **42**, 168), the solution should be titrated with standard sodium hydroxide and the quantity of hydrochloric acid adjusted to that required to form the dihydrochloride (compare equations of the reactions).

Estimation of Ferrocyanides.—Potassium ferrocyanide (standardisation). Found (by *V.M.*): $K_4Fe(CN)_6,3H_2O$ = 99·9, 99·8 %.

Ammonium ferrocyanide was prepared by adding a large excess of alcohol to a solution of the crude salt in the minimum quantity of cold water; after prolonged and vigorous shaking, the salt was thrown out as lustrous, light green, stable plates. It was filtered off, washed with a little alcohol and finally with ether, and dried in the air at the ordinary temperature. *G.M.* Factor = 3·556. Found: $(NH_4)_4Fe(CN)_6$ = 81·9, 82·0%. *V.M.* The salt was estimated by titrating the filtrate with alkali and methyl-red, or by boiling the alkaline solution of the salt until all the ammonia was expelled. After dilution and neutralisation, excess of standard benzidine dihydrochloride solution was added, the precipitate filtered off, and

the filtrate titrated with standard alkali and methyl-orange [Found: $(NH_4)_4Fe(CN)_6$=81·9, 82·1 %. This result was confirmed from a second preparation of the salt. $(NH_4)_4Fe(CN)_6,3\frac{1}{2}H_2O$ requires $(NH_4)_4Fe(CN)_6$, 81·85%]. Williams ("Cyanogen Compounds," Churchill, 1915) assigns $4H_2O$, and Etard and Bémont (*Compt. rend.*, 1885, **100**, 108) $3H_2O$ to the salt precipitated from alcohol.

Magnesium ferrocyanide was purified in the same way as the ammonium salt. There is, however, no difficulty in mixing the aqueous solution with alcohol. *G.M.* Factor = 3·263. Found: $Mg_2Fe(CN)_6$ = 54·5, 54·3%. *V.M.* Found: $Mg_2Fe(CN)_6$ = 54·3, 54·2%. [$Mg_2Fe(CN)_6,12H_2O$ requires $Mg_2Fe(CN)_6$, 54·7%]. The salt, when recrystallised from alcohol, had the same composition [Found: $Mg_2Fe(CN)_6$=54·7%].

Barium ferrocyanide was boiled with a little concentrated potassium carbonate solution until decomposition was complete. The liquid was cooled, diluted to complete the precipitation of the barium carbonate, filtered, and the ferrocyanide in the filtrate estimated as before. *G.M.* Factor = 6·094. Found: $Ba_2Fe(CN)_6$ = 82·1, 81·7%. *V.M.* Found: $Ba_2Fe(CN)_6$ = 81·6, 81·7% [$Ba_2Fe(CN)_6,6H_2O$ requires $Ba_2Fe(CN)_6$, 81·8%]. This salt was also estimated as a soluble ferrocyanide, but bulky solutions were involved [Found: $Ba_2Fe(CN)_6$, 81·8%].

Lead ferrocyanide was prepared by adding cold dilute potassium ferrocyanide in excess to a dilute solution of lead acetate, washing the salt with warm water until free from soluble ferrocyanide, and drying it in the air. In the estimation, the lead was removed with potassium carbonate as in the case of barium, or by saturating a warm solution of the ferrocyanide in a little concentrated sodium hydroxide solution with carbon dioxide and diluting and filtering it. *G.M.* Factor = 7·844. Found: $Pb_2Fe(CN)_6$ = 86·3, 86·3%. *V.M.* Found: $Pb_2Fe(CN)_6$ = 85·8, 86·3%. The salt appears to contain $5\frac{1}{2}$ molecules of water [theory requires $Pb_2Fe(CN)_6$, 86·3%]. The degree of hydration is given as 3, 4, 5, and $6H_2O$ by different investigators.

Zinc ferrocyanide was prepared from zinc sulphate as in the case of the lead salt. Sodium and potassium carbonates convert zinc ferrocyanide partly into a basic salt, so the following method of estimation was adopted. The salt was dissolved in a small excess of sodium hydroxide solution, and yellow ammonium sulphide solution added drop by drop until precipitation was complete. The precipitated zinc sulphide was filtered off and washed with hot water, and the filtrate boiled to expel ammonia. The filtrate and washings were carefully neutralised and cooled. (In most cases a

slight separation of sulphur takes place, but it is unnecessary to remove this. It is also unnecessary to remove any hydrogen sulphide formed. Hydrogen sulphide may be used to precipitate the zinc, but the solution should not be saturated.) After neutralisation the ferrocyanide in the filtrate was estimated as before. *G.M.* Factor = 4·292. Found: $Zn_2Fe(CN)_6 = 79·4$, 79·9%. *V.M.* Found: $Zn_2Fe(CN)_6 = 79·2\%$. [$Zn_2Fe(CN)_6,5H_2O$ requires $Zn_2Fe(CN)_6$, 79·2%]. A specimen of zinc ferrocyanide obtained from the British Drug Houses was found to have the same composition. Friend ("Text-Book of Inorganic Chemistry," IX, p. 2220) gives 3 or 4 H_2O.

Estimation of Ferricyanides.—*Sodium ferricyanide* was purified from a well-agitated, aqueous solution of alcohol. *G.M.* Factor = 3·518. Found: $Na_3Fe(CN)_6 = 88·4$, 88·1%. *V.M.* Found: $Na_3Fe(CN)_6 = 88·7$, 88·7% [$Na_3Fe(CN)_6,2H_2O$ requires $Na_3Fe(CN)_6$, 88·6%].

Potassium ferricyanide (standardisation). *V.M.* Found: $K_3Fe(CN)_6 = 100·0$, 100·2%.

As most ferricyanides are soluble in water, the method is almost generally applicable. In the case of insoluble ferricyanides the metal should be removed by some suitable reagent as outlined for insoluble ferrocyanides.

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[*Received, June 12th*, 1926.]

CCLVI.—*The Rotatory Dispersion of the Esters of Lactic Acid. Part II. The Isomeric Butyl Esters.*

By CHARLES EDMUND WOOD, JOHN EDWARD SUCH, and FRANK SCARF.

PART I of this investigation (J., 1923, **123**, 600) described the rotatory dispersion of the normal esters of lactic acid and was undertaken as a preliminary step to afford a standard of reference for the work now described, *viz.*, the study of the isomeric butyl lactates with special reference to the effect of two simple asymmetric carbon atoms in the molecule.

Specific Rotations.

Considering the first two esters in the following tables, it is clear that the primary branching of the normal carbon chain results in an increase of rotatory power; further branching, as shown in the tertiary ester, brings about a considerable decrease.

Temp. 20°.	λ 6708.	λ 5893.	λ 5461.	λ 5086.	λ 4359.
n-Butyl *l*-lactate	+10·41°	+13·45°	+15·50°	+17·62°	+22·40°
*iso*Butyl *l*-lactate	+11·72	+15·18	+17·55	+20·08	+25·97
tert.-Butyl *l*-lactate	+ 7·76	+ 9·45	+10·93	+12·44	+15·90
dl-sec.-Butyl *l*-lactate	+ 7·50	+ 9·44	+10·74	+12·03	+14·80
d-sec.-Butyl *l*-lactate	+16·02	+20·67	+23·91	+27·42	+35·37
d-sec.-Butyl *d*-lactate	− 1·53	− 1·83	− 1·83	− 1·54	+ 0·75
Temp. 110°.					
n-Butyl *l*-lactate	+11·53	+15·10	+17·68	+20·14	+26·56
*iso*Butyl *l*-lactate	+12·54	+16·48	+19·22	+22·13	+29 32
tert.-Butyl *l*-lactate	+ 8·35	+11·00	+13·00	+14·95	+19·37
dl-sec.-Butyl *l*-lactate	+ 9·86	+12·79	+14·73	+16·60	+20·74
d-sec.-Butyl *l*-lactate	+17·03	+21·90	+25·39	+28·95	+37·13
d-sec.-Butyl *d*-lactate	− 4·52*	− 6·03*	− 6·65*	− 7·05*	− 7·52*

* Temperature 100°.

The inactive secondary ester also shows a decrease of rotatory power to approximately the same extent as the tertiary ester.

Where there are two asymmetric centres of the same sign in the molecule, as in *d-sec.*-butyl *l*-lactate,† the rotation is considerably increased, whilst two asymmetric centres of opposite sign in the molecule, as in *d-sec.*-butyl *d*-lactate, result in a very pronounced decrease in the specific rotation. In each case, the effect is more pronounced for rotations in the violet end of the spectrum.

It is to be noted that the last member of the series is an ester of *dextro-* and not *lævo*-lactic acid, so that the numerical values, and not the sign of rotation (except the value for $[\alpha]^{20°}_{4359}$), can be compared with the values for the other esters.

It has been suggested (Hilditch, *Z. physikal. Chem.*, 1911, **77**, 482) that accumulation of identical radicals upon one carbon atom near the asymmetric centre produces a kind of symmetry resulting in a diminution of rotation. Our results support this idea. Rupe, however (*Trans. Faraday Soc.*, 1914, **10**, 5), cites the case of the molecular rotations of the menthyl esters of monomethyl-, dimethyl-, and trimethyl-acetic acids, where the symmetry of the last has no marked influence on the asymmetric system.

Dispersion Ratios and Dispersion.

The following table shows that the dispersion ratios for the temperatures 20° and 110° (except those for *d-sec.*-butyl *d*-lactate, which exhibits anomalous rotatory dispersion) are sensibly constant.

Temp. 20°.	λ 6708.	λ 5893.	λ 5461.	λ 5086.	λ 4359.
n-Butyl *l*-lactate	0·67	0·87	1	1·14	1·45
*iso*Butyl *l*-lactate	0·67	0·87	1	1·14	1·43
tert.-Butyl *l*-lactate	0·71	0·86	1	1·14	1·45
dl-sec.-Butyl *l*-lactate ...	0·70	0·88	1	1·12	1·38
d-sec.-Butyl *l*-lactate.....	0·67	0·87	1	1·15	1·48
d-sec.-Butyl *d*-lactate ...	0·84	1·00	1	0·84	−4·10

† The esters of *l*-lactic acid are *dextro* rotatory.

Temp. 110°.	λ 6708.	λ 5893.	λ 5461.	λ 5086.	λ 4359.
n-Butyl *l*-lactate	0·66	0·86	1	1·14	1·50
*iso*Butyl *l*-lactate	0·65	0·86	1	1·14	1·51
tert.-Butyl *l*-lactate	0·64	0·85	1	1·15	1·49
dl-sec.-Butyl *l*-lactate ...	0·67	0·87	1	1·13	1·41
d-sec.-Butyl *l*-lactate.....	0·67	0·86	1	1·14	1·47
d-sec.-Butyl *d*-lactate ...	0·68*	0·91*	1*	1·06*	1·13*

* Temperature 100°.

A slight irregularity is observed for the *dl-sec.*-butyl ester, particularly in the region of shorter wave-length. The ratios differ only slightly from the values calculated for the normal alkyl lactates (*loc. cit.*). The ratios $[\alpha]^{\circ}_{4359}/[\alpha]^{\circ}_{5461}$ (except for *d-sec.*-butyl *d*-lactate) lie below the value 1·57, thus indicating complexity of the dispersion curves. The curves obtained by plotting $1/\alpha$ against λ^2 for all these esters show marked curvature. The irregularities noted for *d-sec.*-butyl *d*-lactate are due to the anomalous rotatory dispersion of this ester, by reason of which the ratios may vary considerably.

All the dispersion curves (except those for *d-sec.*-butyl *d*-lactate) are convex towards the axis of zero-rotation. The curves obtained for the *iso-*, *tert.-* and *dl-sec.*-esters are exactly similar in type to those obtained for the *n*-butyl ester, *i.e.*, similar in type to those of the *n*-alkyl lactates. They neither intersect nor show minima; further, each ester exhibits a distinct and similar spreading of the curves on passing to shorter wave-lengths; this holds even in the case of the *dl-sec.*-butyl *l*-ester, which shows that the dextro- and lævo-centres in the inactive secondary radical have no abnormal effect.

The curves for *d-sec.*-butyl *l*-lactate are remarkable for the absence of spreading, being almost parallel lines of convex curvature crossing the diagram, the rotation being considerably increased owing to the molecule containing two optically active centres of the same sign.

The curves for *d-sec.*-butyl *d*-lactate lie almost wholly in the negative region and are concave to the axis of zero-rotation except for light of short wave-length; those for the *l-sec.*-butyl *l*-ester, however, would lie almost wholly in the positive region and would be concave to the axis. Therefore the curvature has been reversed owing to the molecule containing two optically active centres of opposite sign and unequal rotation.

The dispersion of the *n*-alkyl lactates is in agreement with the conditions of Case III (Hunter, J., 1924, **125**, 1198) involving a two-term Drude equation in which $k_0 > k_1$ when $\lambda_0 > \lambda_1$. In this class may be included all the isomeric butyl lactates with the exception of *d-sec.*-butyl *d*-lactate. The type of dispersion is not

changed in either the *dl-sec.*- or the *d-sec.*-butyl *l*-lactates, where there is more than one asymmetric centre in the molecule.

A different type of dispersion is exhibited by *d-sec.*-butyl *d*-lactate which is in accordance with Case IV (Hunter, *loc. cit.*), in which $k_0 < k_1$ when $\lambda_0 > \lambda_1$. The dispersion here is similar in every respect to the anomaly shown by the tartrates, crossing of the axis and minima occurring in certain of the rotation–dispersion curves. The minima move in the usual manner towards the violet end of the spectrum with increase of temperature and ultimately disappear.

According to Tschugaev, one of the factors giving rise to anomalous rotatory dispersion is "the superposition of the partial rotations produced by two asymmetric complexes within the molecule of an active body, the necessary condition being that these partial rotations should be of opposite sign and should possess different dispersion ratios." Up to the present the only substances exhibiting phenomena of this kind which have been carefully studied have contained two fairly complicated centres of activity (Tschugaev, *Ber.*, 1911, **44**, 2023; *Z. physikal. Chem.*, 1913, **85**, 481).

Two of the esters included in this paper, *d-sec.*-butyl *l*-lactate and *d-sec.*-butyl *d*-lactate, afford the simplest examples of compounds containing two asymmetric centres in the molecule, and where the rotations of the asymmetric complexes are of the same sign the rotatory dispersion remains complex in character in common with that of the other isomeric butyl lactates and the *n*-alkyl lactates (except, of course, *d-sec.*-butyl *d*-lactate); when, however, the rotations of the two asymmetric centres are of opposite sign, anomalous dispersion results.

Effect of Change of Temperature.—The temperature effect is small, as is the case with the *n*-alkyl lactates, lines of slight curvature concave to the axis (with the exception of those for *d-sec.*-butyl *l*-lactate) being obtained. Increase of temperature results in an increase in rotation (except in the case of *d-sec.*-butyl *d*-lactate at low temperatures and for short wave-lengths), the increase becoming more pronounced with decrease in wave-length.

Maxima occur in the temperature–rotation curves for *iso*butyl *l*-lactate. A similar observation was made with regard to *n*-butyl *l*-lactate, in which case, however, the maxima persisted farther into the blue end of the spectrum.

Curves for the *d-sec.*-butyl *l*-lactate are of the same general nature, except that they exhibit no maxima and are convex towards the axis of zero-rotation. In the latter respect they differ from all other temperature–rotation curves obtained for the lactates hitherto examined.

The temperature–rotation curves for different wave-lengths for

the *d-sec.*butyl *d*-lactate show only an approach to maxima (for there is no intersection of the rotation dispersion curves), but intersection of these curves takes place in a manner precisely the same as in the cases of methyl and ethyl tartrates. The rotation in the red end of the spectrum for a lower temperature is less than for a higher temperature, but, as the wave-length decreases, the rotation increases more rapidly with temperature and intersection takes place; in addition, the maxima are apparently moving to a higher temperature with decrease of wave-length. Phenomena of the same kind are encountered in certain esters of tartaric acid which are anomalous.

Optical Superposition.

A point of interest with respect to optical superposition arises from the data given in the table on p. 1929. The three esters *d*-butyl *l*-lactate (having two rotations of the same sign, giving a large rotation), *d*-butyl *d*-lactate (having two rotations of opposite sign, giving a small rotation), and *dl*-butyl *l*-lactate (a solution of *d*-butyl *l*-lactate in *l*-butyl *l*-lactate) have a bearing on the validity of van 't Hoff's assumption.

sec.-Butyl *l*-lactates.	λ 6708.	λ 5893.	λ 5461.	λ 5086.	λ 4359.	
½ (*d*- + *l*-)	8·78°	11·25°	12·87°	14·48°	17·31°	Temp. 20°.
dl-	7·50	9·44	10·74	12·03	14·80	
Diff.	1·28	1·81	2·13	2·45	2·51	
½ (*d*- + *l*-)	10·68	13·87	15·91	17·88	22·20	Temp. 100°.
dl-	9·80	12·53	14·38	16·17	20·26	
Diff.	0·88	1·34	1·53	1·71	1·94	

It will be noted that the rotations for the ester (*dl*-alcohol *l*-acid) differ from the mean for the two esters (*d*-alcohol *l*-acid and *l*-alcohol *l*-acid *). The difference is beyond the experimental limits and increases on passing into the blue end of the spectrum. The differences from the mean given by Patterson and Buchanan (J., 1924, **125**, 2579) in the case of the methyl *n*-hexylcarbinyl dimethoxysuccinates also increase on passing from the red to the blue end of the spectrum. These examples indicate that measurements should be taken over as wide a range of wave-lengths as possible.

At the higher temperature, 100°, the differences are somewhat smaller. Our case is open to an objection, since the *dl-sec.*-butyl *l*-lactate is a solution of equal parts of the *d*- and *l*-butyl esters, a disadvantage which has been overcome in the examples selected by Patterson. These lactic esters afford no quantitative vindication of the rule and the values of the rotations calculated for wave-lengths in the neighbourhood of sodium light are outside the limits of experimental error.

* Experimentally the ester *d*-alcohol *d*-acid was obtained.

Hudson (*J. Amer. Chem. Soc.*, 1925, **47**, 265, 543, 873) states that van 't Hoff's principle of optical superposition holds closely for the methylglucosides, galactosides, etc., the maximum deviation being about 4%, but his calculations are based on rotations for sodium light.

Experimental.

iso*Butyl* l-*Lactate*.—25 G. of dry zinc ammonium *l*-lactate, 80 c.c. of *iso*butyl alcohol (b. p. 109°/748 mm.), and 10·8 c.c. of concentrated sulphuric acid were heated together on a water-bath for 6 hours. The reaction mixture was treated similarly to *n*-hexyl *l*-lactate (Wood, Scarf, and Such, *loc. cit.*). After four fractional distillations the ester had b. p. 73·1°/13 mm. Yield 11 g. (38% of the theoretical).

The ester had a penetrating fragrant odour. In the following table its physical constants as found by the authors (W. S. and S.) are compared with those (G. and W.) found by Guye and Wassmer (*J. Chim. phys.*, 1903, **1**, 257).

	B. p. /13 mm.	$d_{4^\circ}^{18^\circ}$.	$d_{4^\circ}^{25^\circ}$.	$[\alpha]_D^{18^\circ}$.	$[\alpha]_D^{18^\circ}$ (calc.).	$[M]_D^{18^\circ}$.
(G. & W.)	72—75°	0·9760	0·9390	13·03°	15·4°	22·5°
(W. S. & S.)	73·1	0·9755	0·9378	15·13	—	22·18

Densities determined:

t°	8·3°	29·9°	57·1°	91·5°	120·5°	139·9°
$d_{4^\circ}^{t^\circ}$	0·9849	0·9636	0·9356	0·9015	0·8717	0·8523

The ester shows maxima in the temperature–rotation curves for longer wave-lengths and exhibits complex rotatory dispersion.

The following *specific rotations*—and all others recorded in this paper—were determined in a 1 dcm. tube.

	$[\alpha]_\lambda^{t^\circ}$.						
λ.	14·1°.	22·1°.	48·2°.	77·6°.	97·7°.	121·6°.	138·0°.
6708	+11·64°	+11·74°	+12·02°	+12·26°	+12·49°	+12·59°	+12·47°
6563	12·15	12·26	12·29	12·92	13·11	13·22	13·15
6438	12·67	12·77	13·10	13·47	13·67	13·80	13·74
6152	13·85	13·98	14·37	14·78	15·02	15·20	15·19
5893	15·08	15·21	15·65	16·09	16·37	16·60	16·64
5590	16·70	16·86	17·39	17·89	18·21	18·51	18·61
5324	18·28	18·46	19·11	19·67	20·04	20·40	20·53
5086	19·93	20·13	20·84	21·46	21·91	22·33	22·53
4861	21·54	21·76	22·52	23·29	23·79	24·33	24·60
4678	22·97	23·20	24·06	24·92	25·48	26·05	26·44
4455	24·89	25·16	26·13	27·12	27·77	28·53	28·90
4359	25·75	26·04	27·03	28·10	28·89	29·71	30·24
$d_{4^\circ}^{t^\circ}$	0·9791	0·9711	0·9445	0·9155	0·8950	0·8706	0·8541

tert.-*Butyl* l-*Lactate*.—*tert.*-Butyl alcohol, m. p. 25°, b. p. 82°/760 mm., was prepared in 78% yield by the Grignard reaction from magnesium methyl iodide and methyl acetate (Grignard, *Compt.*

rend., 1901, **132**, 336), with certain modifications in apparatus (see *J. Soc. Chem. Ind.*, 1923, **42**, 137T). Considerable difficulty was experienced in the preparation of this ester. The following methods were tried with the results indicated:

(1) Similar to the preparation of the *n*-alkyl lactates. Yield small owing to the decomposition of the alcohol by the acid.

(2) Esterification by hydrochloric acid under various conditions. Scarcely any ester was formed. The alcohol was attacked and a chloro-compound produced.

(3) A cyclic method (Frankland and Aston, J., 1901, **79**, 511) in which free *l*-lactic acid was employed. The yield was poor.

(4) A modification of the sulphuric acid method was adopted which gave better but by no means good yields. Three specimens of the ester were prepared in this way, the rotations of which, after vacuum distillation, were identical.

27 G. of dry zinc ammonium *l*-lactate were mixed with 25 g. of *tert.*-butyl alcohol, and 17 g. of concentrated sulphuric acid were slowly added with shaking. The mixture was heated at 60—70° for 7 hours. During the esterification a further 10 g. of the alcohol were added in small portions. The subsequent treatment was similar to that described for the *iso*butyl ester. After four fractional distillations 7 g. (22% of theoretical) of the ester were obtained, which had b. p. 46—47°/9 mm., $[\alpha]_D^{20°}$ + 9·48°, $[M]_D^{20°}$ + 13·84°, $d_4^{20°}$ 0·9139. No comparative data are available (equivalent weight by saponification, 146·4. Calc.: 146·1).

Densities determined:

$t°$	0°	16·1°	48·8°	80·8°	112·7°
$d_4^{t°}$	0·9328	0·9170	0·8865	0·8553	0·8242

The ester exhibits complex rotatory dispersion.

	$[\alpha]_\lambda^{t°}$.					
λ.	3°.	25°.	45°.	67·7°.	88·1°.	111·1°.
6708	+ 7·50°	+ 7·82°	+ 8·03°	+ 8·20°	+ 8·27°	+ 8·37°
6563	7·71	8·05	8·34	8·48	8·59	8·74
6438	7·93	8·27	8·63	8·82	8·95	9·10
6152	8·52	8·85	9·25	9·61	9·88	10·06
5893	9·16	9·55	9·95	10·37	10·68	11·04
5590	10·09	10·56	11·03	11·57	12·04	12·45
5461	10·48	11·02	11·60	12·10	12·61	13·07
5324	10·99	11·61	12·20	12·76	13·27	13·80
5086	11·92	12·59	13·19	13·85	14·42	15·01
4861	12·87	13·66	14·38	15·00	15·67	16·37
4678	13·66	14·54	15·26	15·99	16·64	17·41
4455	14·65	15·60	16·43	17·21	17·95	18·75
4359	15·10	16·08	17·00	17·91	18·68	19·41
$d_4^{t°}$	0·9298	0·9090	0·8899	0·8681	0·8485	0·8260

d-sec.-*Butyl* l-*Lactate*.—The racemic *sec.*-butyl alcohol was obtained by the interaction of acetaldehyde and magnesium ethyl bromide. Resolution of the alcohol was effected by the method described by Pickard and Kenyon (J., 1912, **101**, 620) with slight modifications. The final product of *d-sec.*-butyl brucine phthalate had m. p. 159° (Pickard and Kenyon give 155°). The *d-sec.*-butyl hydrogen phthalate obtained from this salt had m. p. 48° and $[\alpha]_D^{20°}$ + 39·5° (alcoholic solution). Pickard and Kenyon give m. p. 46—47° and $[\alpha]_D^{20°}$ + 38·9°. On hydrolysis 7·5 g. of *d-sec.*-butyl alcohol were obtained of b. p. 99°/760 mm. and $[\alpha]_D^{20°}$ + 13·89°.

Preliminary investigations showed that the best method for preparing higher lactic esters when only a small quantity of the alcohol was available was by intermolecular change from ethyl *l*-lactate. 17 G. of ethyl *l*-lactate, 7·5 g. of *sec.*-butyl alcohol, and 0·1 c.c. of concentrated sulphuric acid were maintained at 90—100° for 6 hours. The mixture was then treated as in the preparation of the other butyl esters, and yielded, after four fractional distillations, 7 g. of *d-sec.*-butyl *l*-lactate, b. p. 59°/7 mm. (oil-bath temperature, 90°): $[\alpha]_D^{20°}$ + 20·67°, $[M]_D^{20°}$ + 30·18°, $d_4^{20°}$ 1·0041 (Found: C, 57·6; H, 9·6; *M*, by saponification, 145·6. $C_7H_{14}O_3$ requires C, 57·5; H, 9·6%; *M*, 146·1).

After hydrolysis of the ester the alcohol isolated had a rotation identical with that of the original.

Densities determined:

$t°$	0°	18·03°	49·5°	82·3°	140·0°
$d_4^{t°}$	1·0247	1·0063	0·9732	0·9377	0·8789

The ester exhibits complex rotatory dispersion.

	$[\alpha]_\lambda^{t°}$.					
λ.	2·1°.	23·9°.	51·0°.	74·1°.	110·8°.	137·8°.
6708	+15·99°	+16·03°	+16·23°	+16·45°	+17·08°	+17·58°
6563	16·70	16·73	16·93	17·15	17·83	18·32
6438	17·31	17·37	17·59	17·78	18·44	18·96
6152	18·98	19·03	19·21	19·47	20·11	20·66
5893	20·61	20·69	20·92	21·24	21·92	22·48
5590	22·85	22·94	23·20	23·49	24·30	24·92
5461	23·81	23·96	24·19	24·63	25·42	26·05
5324	25·00	25·14	25·42	25·79	26·66	27·28
5086	27·32	27·46	27·79	28·13	28·96	29·62
4861	29·65	29·81	30·13	30·51	31·33	32·03
4678	31·69	31·83	32·14	32·51	33·41	34·14
4455	34·07	34·25	34·57	35·05	36·01	36·84
4359	35·22	35·43	35·76	36·25	37·18	37·98
$d_4^{t°}$	1·0227	1·0000	0·9717	0·9476	0·9094	0·8813

d-sec.-*Butyl* d-*Lactate*.—Attempts to obtain zinc ammonium *d*-lactate by the use of the alkaloids strychnine, brucine, codeine, narcotine, quinine and cinchonine gave negative results. The

following method, an adaptation of that used to obtain the lævo-variety, was finally adopted.

One equivalent of morphine was added to slightly less (2%) than two equivalents of *N*-lactic acid, and the less soluble morphine *l*-lactate was removed by alternate evaporation and crystallisation. The resulting solution contained *d*-lactic acid and a little morphine *d*-lactate, all the *l*-lactic acid having been removed as the morphine salt. Ammonia was added, and the solution was filtered, boiled with zinc oxide, filtered again, and crystallised. Recrystallisation from dilute ammonia yielded pure zinc ammonium *d*-lactate, $[\alpha]_D^{17°}$ — 10·05° (2·5 g. of salt in 50 c.c. of dilute ammonia).

d-sec.-Butyl *d*-lactate was obtained by intermolecular change from ethyl *d*-lactate, the latter ester being obtained from the zinc ammonium *d*-lactate. 8 G. of ethyl *d*-lactate ($[\alpha]_D^{19°}$ — 11·26°, b. p. 53°/15 mm.), 8 g. of *d-sec.*-butyl alcohol, and 0·1 c.c. of concentrated sulphuric acid were heated on a water-bath for 12 hours. The mixture was then treated as in previous esterifications. Yield 5 g. of ester, b. p. 69—70°/16 mm. (oil-bath temperature, 100°), which gave constant rotation after four fractionations.

The ester had $[\alpha]_D^{20°}$ — 1·83°, $[M]_D^{20°}$ — 2·67°, $d_4^{20°}$ 1·0047 (Found: C, 57·5; H, 9·7%; *M*, by saponification, 146·5).

After hydrolysis of the ester, the alcohol isolated had a rotation identical with that of the original.

Densities determined:

$t°$	0°	15·2°	39·2°	70·5°	98·0°
$d_4^{t°}$	1·0255	1·0095	0·9847	0·9528	0·9243

The ester exhibits anomalous rotatory dispersion.

	$[\alpha]_\lambda^{t°}$.				
λ.	2·5°.	17·0°.	44·5°.	76·5°.	100·0°.
6708	−0·42°	−1·34°	−2·84°	−4·01°	−4·52°
6563	−0·51	−1·45	3·00	4·25	4·83
6438	−0·58	−1·51	3·13	4·53	5·10
6152	−0·57	−1·60	3·37	4·95	5·60
5893	−0·50	−1·59	3·60	5·35	6·03
5590	−0·26	−1·55	3·78	5·67	6·46
5461	−0·12	−1·51	3·87	5·80	6·65
5324	+0·06	−1·39	3·90	5·88	6·81
5086	+0·50	−1·17	3·96	6·05	7·05
4861	+1·00	−0·84	3·92	6·13	7·22
4678	+1·65	−0·56	3·98	6·18	7·36
4455	+2·24	−0·06	3·51	6·18	7·50
4359	+2·60	+0·17	3·37	6·17	7·52
$d_4^{t°}$	1·0230	1·0079	0·9797	0·9469	0·9225 (extrapolated)

At 120° the rotatory power of the ester indicated decomposition or racemisation.

dl-sec.-*Butyl* l-*Lactate*.—The ester was obtained by intermolecular change from active ethyl *l*-lactate by the method described under *d-sec.*-butyl *l*-lactate. 17 G. of ethyl *l*-lactate, 15 g. of *dl-sec.*-butyl alcohol, and 0·2 c.c. of concentrated sulphuric acid were heated at 95° for 5 hours, the mixture being subsequently treated as in the case of the other butyl esters. A 50% yield of *dl-sec.*-butyl *l*-lactate was obtained, which after four fractional distillations had b. p. 65—67°/12 mm. (oil-bath temperature, 100°), $[\alpha]_D^{20°}$ +9·45°, $[M]_D^{20°}$ + 13·80°, $d_4^{20°}$ 0·9968 (Found: C, 57·5; H, 9·7%; *M*, by saponification, 145·8).

The alcohol obtained after hydrolysis of the ester proved to be inactive.

Densities determined:

$t°$	−13°	1°	15·4°	53°	74·2°	88·5°	132°
$d_4^{t°}$	1·0313	1·0170	1·0015	0·9617	0·9395	0·9241	0·8780

The ester exhibits complex rotatory dispersion.

	$[\alpha]_\lambda^{t°}$.					
λ.	−10·8°.	0°.	21·9°.	56·5°.	86·6°.	125·8°.
6708	+ 6·35°	+ 6·79°	+ 7·57°	+ 8·69°	+ 9·56°	+10·00°
6563	6·62	7·11	7·87	9·02	9·93	10·42
6438	6·87	7·28	8·15	9·41	10·29	10·87
6152	7·37	7·83	8·81	10·19	11·18	11·96
5993	7·94	8·47	9·51	11·05	12·12	13·11
5590	8·61	9·20	10·42	12·16	13·35	14·50
5461	8·95	9·60	10·84	12·66	13·90	15·19
5324	9·31	9·99	11·31	13·27	14·57	16·63
5086	9·92	10·69	12·12	14·31	15·69	17·08
4861	10·50	11·34	13·01	15·36	16·88	18·35
4678	10·99	11·90	13·73	16·25	17·82	19·47
4455	11·62	12·58	14·59	17·27	19·00	20·73
4359	11·92	12·90	15·01	17·80	19·56	21·42
$d_4^{t°}$	1·0296	1·0180	0·9948	0·9579	0·9272	0·8847

Summary.

1. In the isomeric butyl lactates, the *iso*butyl ester shows an increase whilst the tertiary and inactive secondary butyl esters show a considerable decrease in rotation. Enhanced rotation results when there are two asymmetric centres of the same sign in the molecule (*d-sec.*-butyl *l*-lactate). Pronounced decrease in rotation occurs when there are two asymmetric centres of opposite sign in the molecule (*d-sec.*-butyl *d*-lactate).

2. All the esters examined are normal and complex with the exception of *d-sec.*-butyl *d*-lactate, which shows anomalous rotatory dispersion.

3. The effect of temperature on the rotation is in all cases small. Maxima occur in the rotation–temperature curves for the *iso*butyl

ester and intersections (similar in type to those found in several alkyl tartrates) take place in those for the anomalous ester, *d-sec.*-butyl *d*-lactate.

The authors desire to express their appreciation of the considerable help rendered by Mr. L. W. Needham in the experimental work involved in this paper.

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EDGBASTON. [*Received, May 26th,* 1926.

CCLVII.—*Studies of Dynamic Isomerism. Part XXII. Methyl Alcohol as an Amphoteric Solvent for the Mutarotation of the Sugars.*

By IRVINE JOHN FAULKNER and THOMAS MARTIN LOWRY.

SINCE oxygenated solvents, such as ethyl acetate, acetone, and cresol, and even a nitrogenous base like pyridine, have been proved to be inert (J., 1925, **127**, 1385, etc.), water has for a brief period occupied a unique position as the only compound which could with reasonable confidence be classed as a " complete catalyst " for the mutarotation of the sugars.* Our theory of mutarotation suggested, however, that other amphoteric compounds might possess catalytic properties, such as we have already recorded in dry mixtures of pyridine and cresol (J., 1925, **127**, 2883). The most obvious compounds to test were the alcohols, which are certainly amphoteric in the sense that they can liberate either hydrogen or hydroxyl to suitable chemical agents, but which do not necessarily possess sufficiently strong acidic and basic properties to enable them to act as complete catalysts for the mutarotation of the sugars. Since, however, the residual activity of the most highly purified solvents can always be attributed to imaginary impurities, direct experiments can only lead to conclusive results when the compound is *not* a catalyst; thus, our earlier experiments (J., 1925, **127**, 1396) only enabled us to assert that *if* methyl alcohol is a complete catalyst, its activity cannot be greater than 1/30 of that of water. In the present experiments, therefore, we have sought to reach a definite conclusion by finding out whether methyl alcohol is sufficiently basic to act as a complete catalyst when mixed with cresol, and sufficiently acidic to act as a complete catalyst with pyridine. The

* The reservation still holds, however, that " if the solution could by extreme purification be rendered non-conducting, it is possible that the mutarotation would not take place " (J., 1903, **83**, 1320).

positive results recorded below enable us to conclude that the alcohol must also be capable of acting as a complete catalyst when used alone, although we can now assert that its catalytic activity is less than 1/60 of that of water.

EXPERIMENTAL.

(a) *Direct Method.*—The sugar used was tetramethyl glucose, the purity of which had been tested as already described (this vol., p. 721; compare J., 1925, **127**, 1387, footnote). We have already recorded (*ibid.*, p. 1397) a velocity coefficient of 0·00039 for the mutarotation of this sugar in a sample of methyl alcohol containing about 0·5% of water, as compared with one of 0·0128 for pure water (this vol., p. 722); the corresponding value for a glucose of normal purity was 0·00060. A sample of methyl alcohol specially purified by Hartley for measurements of electrical conductivity, and very kindly sent to us by him in a sealed flask, has now been found to give an almost identical velocity coefficient, viz., 0·00041, when used as a solvent for the mutarotation of tetramethyl glucose. Since the same low velocity coefficient was given by our own, obviously wet, sample of methyl alcohol, it is clear that intensive drying is probably not the most important factor in the process of reducing the catalytic activity of the alcohol to a minimum. This conclusion is in accord with our recent observations on aqueous acetone (this vol., p. 720), as well as with the fact that, in the lower range of concentrations, the addition of 1% of water to methyl alcohol produces an average increase of less than 0·0001 in the velocity coefficient of mutarotation of tetramethyl glucose in this solvent.

In the present instance a more drastic purification was attempted. Using a part of Hartley's method, a litre of methyl alcohol was first purified by boiling it for 3 hours with 5% of its weight of sodium hydroxide, fractionating, and treating the product with successive quantities of a mercury–aluminium couple, until no further action took place. Since the alcohol then had a distinct odour of methylamine, it was distilled from succinic acid in order to remove basic impurities, and finally from a fresh mercury–aluminium couple, in order to remove any water which might have been produced by esterification of the succinic acid. The product gave the lowest velocity coefficient that has yet been recorded, namely, 0·00018 (Table I A). In order to determine, however, whether the velocity could be lowered still further, 50 c.c. of the purified alcohol were sealed up at a pressure of 10 cm. Hg in an all-glass apparatus, and distilled over phosphorus pentoxide at laboratory temperature by immersing the receiver in liquid air. By this means a sample

was obtained which was dry and free from basic impurities, as well as from substances of higher boiling point, which would be left behind by distillation at this temperature. The product of this further purification gave a velocity coefficient of 0·00022 (Table I B).

It is possible that in the future even lower values may be recorded; but, in view of the concordance of the velocities before and after the final stage of the purification, it is reasonable to think that the velocity coefficient will not be reduced much below 0·0002. This conclusion is supported by the fact that a solution which had been stored in a silica flask for 48 hours showed the same rotation (within 0·03°) as the part of the solution which had been transferred to the glass polarimeter tube; and that, even in the most highly purified sample, mutarotation began immediately, without any lag or period of induction, showing that it was due to the solution itself and not to impurities derived from the containing vessels.

TABLE I.

The Effect of Intensive Drying on the Velocity of Mutarotation of Tetramethyl Glucose in Methyl Alcohol.

(5% Solution in 2 dcm. tube at 20°.)

(A) Methyl alcohol dried with Hg–Al couple.			(B) Methyl alcohol dried with P_2O_5.		
Time.	a_{5461}.	k.*	Time.	a_{5161}.	k.*
5	12·06°	—	10	11·94°	—
40	12·04	—	130	11·89	0·00018
1410	11·56	0·00020	250	11·83	0·00022
4320	11·07	0·00017	420	11·78	0·00020
6060	10·78	0·00018	660	11·71	0·00019
7260	10·60	0·00019	1290	11·50	0·00020
Final.	10·09	—	1530	11·36	0·00022
	Mean	0·00018	1770	11·29	0·00022
			2880	11·00	0·00022
			3180	10·92	0·00022
			4320	10·70	0·00022
			Final.	9·96	—
				Mean	0·00022

* $k = 1/t \,.\, \{\log (a_0 - a_\infty) - \log (a_t - a_\infty)\}$; t in minutes.

In the case of *ethyl alcohol* we have been able without taking any elaborate precautions, to reduce the velocity of mutarotation to 0·00016 by mere distillation of the solvent with lime (Table II); moreover, in spite of the smallness of the velocity coefficient, the mutarotation of the solution again started immediately, without any lag or period of induction. Since this velocity coefficient is eighty times smaller than for water (as compared with sixty times in the case of methyl alcohol) it is likely that even lower values may be reached in the higher homologues; but since all the alcohols are more or less amphoteric, we must suppose that they are all

capable, in a larger or smaller degree, of acting as catalysts for the mutarotation of the sugars.

TABLE II.

Mutarotation of Tetramethyl Glucose in Ethyl Alcohol.

(5% Solution in 2 dcm. tube at 20°.)

Time.	a.	k.*	Time.	a.	k.*
10 min.	11·86°	—	5760 min.	10·71°	0·00015
90	11·81	—	7200	10·50	0·00016
1380	11·46	0·00017	8640	10·34	0·00017
1920	11·36	0·00016	11,520	10·08	0·00016
2820	11·16	0·00016	Final	9·90	—
4380	10·87	0·00016	(13 days).		

Mean 0·00016

(b) *Indirect Method.*—The methods used to purify the pyridine and cresol, and to determine the velocity of mutarotation in the mixed solvents, have already been described (J., 1925, **127**, 2884). The methyl alcohol was the same sample as that used for the mutarotation recorded in Table I A. The results of the experiments are in Table III and Fig. 1.

TABLE III.

Mutarotation of Tetramethyl Glucose in Mixtures of

(A) Methyl alcohol and cresol.		(B) Methyl alcohol and pyridine.	
Methyl alcohol.	k.*	Methyl alcohol.	k.*
100%	0·0002	100%	0·0002
75	0·0008	90	0·0182
50	0·0013	80	0·0284
25	0·0018	60	0·035
10	0·0013	40	0·0216
0	0·0005	20	0·0089
		0	0·003

* $k = 1/t \,.\, \{\log (a_0 - a_\infty) - \log (a_t - a_\infty)\}$; t in minutes.

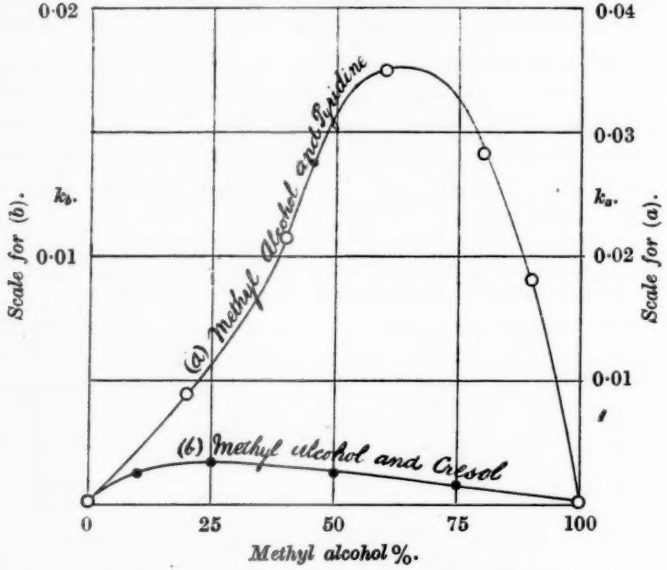
A very striking maximum was recorded in the series of mixtures of methyl alcohol with pyridine at about 60% of the former, where the velocity was about three times as great as in pure water, although only about one-eighth as great as in the most efficient mixture of pyridine and water. This high velocity of mutarotation cannot be due to traces of water in the alcohol, since it requires nearly 20% of water to develop a similar degree of activity in aqueous pyridine; and it would be even more difficult to imagine that it was due to some substance other than water or methyl alcohol, in view of the enormous activity which it would be necessary to postulate in this hypothetical acidic impurity, which must, moreover, be supposed to have survived a prolonged treatment with an alkaline drying agent. There can therefore be no doubt that a mixture of pyridine

and methyl alcohol is a complete catalyst for the mutarotation of tetramethyl glucose.

In the case of methyl alcohol and cresol, the evidence is less striking; but we have nevertheless been able to record the occurrence of a definite maximum velocity of mutarotation in a mixture of 4 parts of cresol with 1 part of methyl alcohol (Fig. 1). Here again, we have to consider whether this increased velocity can be attributed to the presence of impurities, and in particular to water, or to some

FIG. 1.

Velocity of mutarotation of tetramethyl glucose in mixtures of methyl alcohol with pyridine and cresol.



basic impurity, which could play the part of pyridine in converting the cresol into a complete catalyst. The method of purification appears to rule out the possible presence of bases; and since 4% of water would be required in order to develop the velocity of mutarotation actually produced by 20% of methyl alcohol, the maximum which we have observed cannot be explained by the possible presence of traces of water in the "dry" solvent. We are therefore obliged to conclude again that a mixture of methyl alcohol with cresol is a complete catalyst for the mutarotation of tetramethyl glucose.

Summary.

(*a*) Purified methyl alcohol, which gave a velocity coefficient of 0·00018 when used as a solvent for the mutarotation of tetramethyl

glucose, gave a maximum velocity coefficient of 0·0018 when mixed with three times its weight of cresol and of 0·035 when mixed with two-thirds of its weight of pyridine. Since methyl alcohol is sufficiently acidic to form a complete catalyst with pyridine, and sufficiently basic to form a complete catalyst with cresol, it must also be able to act alone as an amphoteric solvent to promote the mutarotation of the sugars.

(*b*) The velocity of mutarotation of tetramethyl glucose in purified ethyl alcohol has been reduced to 0·00016 or about eighty times less than the velocity in water. Since the chemical properties of ethyl alcohol are similar to those of methyl alcohol, it is probable that a part of this velocity is again due to the solvent itself.

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CCLVIII.—*Isomeric Phenylserines.*

By MARTIN ONSLOW FORSTER and KESHAVIAH ASWATH NARAIN RAO.

FROM several quarters in recent years currency has been given to the suggestion that the protein molecule does not depend entirely on the polypeptide type of anhydride-structure; the diketopiperazine ring is now recognised as a probable unit in the aggregation of groups. Notably Abderhalden has demonstrated in proteins the presence of preformed diketopiperazines, and the production of picrorocellin by an organism so lowly as a lichen gains thereby an added interest.

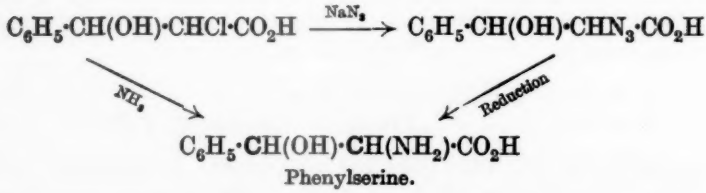
In representing picrorocellin by a structural formula (Forster and Saville, *J.*, 1922, **121**, 818), the position of the *N*-methyl group remained uncertain, and the most promising method of justifying the constitution

$$\begin{array}{l} C_6H_5\cdot CH(O\cdot CH_3)\cdot CH\cdot N(CH_3)\cdot CO \\ \qquad\qquad\qquad\qquad\quad | \qquad\quad | \\ \qquad\qquad\qquad\qquad CO—NH—CH\cdot CH(OH)\cdot C_6H_5 \end{array}$$

appeared to be synthesis from the appropriate amino-acids. For the above constitution, these would be α-methylamino-β-methoxy-β-phenylpropionic acid, $C_6H_5\cdot CH(O\cdot CH_3)\cdot CH(NH\cdot CH_3)\cdot CO_2H$, and α-amino-β-hydroxy-β-phenylpropionic acid (phenylserine), $C_6H_5\cdot CH(OH)\cdot CH(NH_2)\cdot CO_2H$, but although the latter compound is readily available we have failed to convert it into the corresponding diketopiperazine, of which picrorocellin is the *ON*-dimethyl derivative. Nevertheless, as will be shown later, there is evidence that a diketopiperazine is formed when phenylserine is heated at the temperature of decomposition.

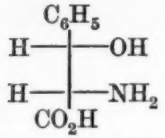
While accumulating the phenylserine required for these experiments, we have encountered an isomeride which appears to have escaped notice, or, if recognised, to have been wrongly described as phenyl*iso*serine. Phenylserine was first prepared by Erlenmeyer, jun. (*Ber.*, 1892, **25**, 3445; Erlenmeyer and Früstück, *Annalen*, 1894, **284**, 36; Erlenmeyer, *ibid.*, 1899, **307**, 84), as the benzylidene derivative arising from glycine condensed with benzaldehyde in aqueous-alcoholic sodium hydroxide; the free amino-acid was observed anhydrous and hydrated, decomposing at the m. p., which was given variously as 196°, 195—196°, and 190° in the former condition and 193—194° or 192—193° in the latter. In the last of the above-quoted papers, Erlenmeyer claims to have recognised in one of his experiments a second form of the acid, decomposing at 187—188°; but the substance was not analysed, and further reference to it has not been made by any other investigator. Phenylserine was more recently obtained by Rosemund and Darnsaft (*Ber.*, 1919, **52**, 1734) from glycine ester and benzaldehyde with sodium in ether, and was stated to melt at 192°. Using Erlenmeyer's process, we obtained anhydrous phenylserine with m. p. 200—202° (decomposition).

Owing to initial difficulties in applying this method, we meanwhile prepared phenylserine by reducing α-triazo-β-hydroxy-β-phenylpropionic acid (Forster and Saville, J., 1922, **121**, 2600) with ammonium sulphide. Thus obtained, the amino-acid was quite distinct from Erlenmeyer's, having m. p. 230—232° (decomposition) when anhydrous, and 213° in the hydrated form. Subsequently, the same acid was produced by the action of concentrated ammonia on cinnamic acid chlorohydrin:

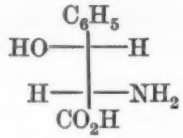


Phenylserine.

The production of two distinct individuals finds a simple explanation in the two dissimilar centres of asymmetry possessed by phenylserine. As represented above, this amino-acid may occur in two racemic forms, each comprising an optically active antipodal pair. Allocation of the appropriate configuration to the isomeric phenylserines follows from consideration of the origin and properties of these compounds, of which we believe the new acid to be the *cis*-modification and Erlenmeyer's to have the *trans*-configuration:



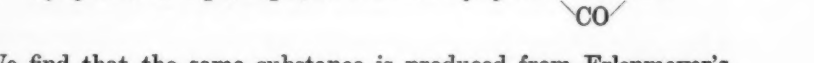
cis-Phenylserine, m. p. 230—232°.



trans-Phenylserine, m. p. 200—202°.

Among the considerations leading to this conclusion is the fact that although addition of chlorine and bromine to cinnamic acid produces externally compensated stereoisomerides (*Ber.*, 1894, **27**, 2039; 1895, **28**, 2235), the action of hypochlorous and hypobromous acids appears to be unidirectional (Read and Andrews, J., 1921, **119**, 1775). At no stage in the sequence, cinnamic acid : chlorohydrin : triazohydrin : phenylserine, is there any experimental evidence of more than one racemic dihydrocinnamic acid derivative being formed.

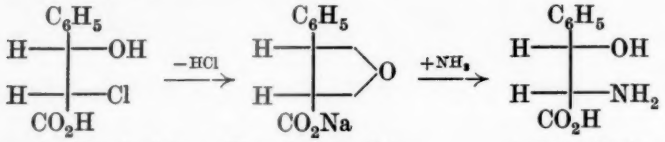
It is thus natural to expect that the hydroxyl and amino-groups in the phenylserine from this source will be found to have the *cis*-relationship, and this is established by comparing the properties of the two isomerides. Erlenmeyer, for instance, heated his phenylserine with benzoic anhydride and obtained the " benzoylaminocinnamic acid lactimide " (yellow, m. p. 164°) insoluble in sodium hydroxide and identical with the product of condensing benzaldehyde with hippuric acid :



We find that the same substance is produced from Erlenmeyer's acid by a much milder method, namely, action of benzoyl chloride suspended in sodium carbonate solution, thus emphasising the surprising facility with which removal of water takes place when favoured by the *cis*-relationship of the hydrogen atom and the hydroxyl group in *trans*-phenylserine. On the other hand, *cis*-phenylserine by the same process yields an undehydrated benzoyl derivative (colourless : m. p. 197°) which is freely soluble in sodium carbonate and fails to pass into the lactimide; the latter was not formed even on heating *cis*-phenylserine with benzoic anhydride. Similarly, the *O*-methyl derivative of *cis*-phenylserine, prepared by reducing the corresponding triazo-compound (Forster and Saville, *loc. cit.*), readily yields a benzoyl derivative (colourless, m. p. 208°) which dissolves in sodium carbonate and resists conversion into the lactimide.

Further support to the foregoing representation of the isomeric phenylserines follows from the action of ammonia on sodium

phenyloxyacrylate, arising from cinnamic acid chlorohydrin by removal of hydrogen chloride:



Cinnamic chlorohydrin. Phenyloxyacrylate. *cis*-Phenylserine.

Erlenmeyer (*Annalen*, 1892, **271**, 155) erroneously ascribed to the product of this action the constitution of phenyl*iso*serine, $C_6H_5{\cdot}CH(NH_2){\cdot}CH(OH){\cdot}CO_2H$, on the ground that its properties differed from those of the phenylserine he obtained from glycine and benzaldehyde. He described it as melting at 220—221°, and announced his intention of confirming the constitution by reducing *iso*nitrosophenylpyruvic acid,

$$C_6H_5{\cdot}C(:NOH){\cdot}CO{\cdot}CO_2H \longrightarrow C_6H_5{\cdot}CH(NH_2){\cdot}CH(OH){\cdot}CO_2H.$$

As the matter does not appear to have been carried further, however, we can only conclude that phenyl*iso*serine may be erased from the literature, the substance described under that name being incompletely purified *cis*-phenylserine. Erlenmeyer's whole treatment of the subject is most bewildering. In a final paper with Barkow (*Ber.*, 1906, **39**, 793) he states that "phenyl*iso*serine," as obtained by the action of cold ammonia on cinnamic acid chlorohydrin, decomposes at 241°, and that sodium phenyloxyacrylate when heated with ammonia yields only the phenyl*iso*serine melting at 220—221°. He leaves the reader to suppose that he regards them as distinct, but at the conclusion of the paper he refers to the less fusible substance as "phenylserine," stating that the corresponding active compound has not hitherto been obtained crystalline; he then records a rotation for the copper salt without indicating how the substance was resolved, announcing that a detailed communication would follow in another place. We have searched in vain for this communication, although 15 years elapsed before the author's death.

During the course of these experiments we have made several attempts to prepare α-triazocinnamic acid, $C_6H_5{\cdot}CH{:}CN_3{\cdot}CO_2H$, but without success. Knowing the close attachment of halogen to unsaturated carbon, we did not expect directly to replace chlorine or bromine in α-chloro- or α-bromo-cinnamic acid by the triazo-group, but until the configuration of *cis*-phenylserine was appreciated it did seem possible to remove the elements of water from α-triazo-β-hydroxy-β-phenylpropionic acid, and persistent failure to accomplish this provides additional evidence in favour of the

cis-configuration. The result, nevertheless, is most disappointing, because α-triazocinnamic acid, by the ammonium sulphide method of reduction, might conceivably yield α-aminocinnamic acid, belonging to a class of substances which have hitherto eluded all attempts to prepare them.

Experimental.

cis-α-*Amino*-β-*hydroxy*-β-*phenylpropionic Acid* (cis-*Phenylserine*).—(a) *From* α-*triazo*-β-*hydroxy*-β-*phenylpropionic acid.* The triazo-derivative (10 g.) dissolved in dilute ammonia was treated with excess of ammonium sulphide, freshly prepared, when a transient, greenish-black precipitate was formed and almost immediately dissolved. The temperature rose, gas was liberated freely, and the colour diminished. At the conclusion of effervescence, the liquid was evaporated to dryness and the product dissolved in water, filtered from sulphur, again evaporated to dryness, and acidified with dilute acetic acid. Final evaporation left a colourless residue of the amino-acid with ammonium acetate which was removed by 95% alcohol, cis-*phenylserine* (7·5 g.) remaining as a white powder. It is moderately easily soluble in water and is best purified by precipitation with absolute alcohol from a saturated aqueous solution, crystallising in clustered needles, m. p. 230—232° (decomp.) (Found: N, 7·8. $C_9H_{11}O_3N$ requires N, 7·7%). Slow separation from the aqueous alcohol yields the hydrated form, m. p. 213°, and the yellow, resinous material arising from decomposition at the higher temperature is freely soluble in alcohol, but does not yield a diketopiperazine in crystalline form. A concentrated aqueous solution of the amino-acid, when boiled with copper carbonate, gives a sparingly soluble blue salt.

(b) *From cinnamic acid chlorohydrin.* The chlorohydrin (5 g.) was shaken with concentrated ammonia until dissolved, and set aside during one week. The residue left on evaporation was dissolved in dilute acetic acid, and the pasty residue from evaporation of this liquid was extracted with 95% alcohol, which left *cis*-phenylserine (3 g.) undissolved. Purified as above, the product was identical with the foregoing according to the unaltered m. p. of a mixture, and of the mixed benzoyl derivatives (see below).

(c) *From sodium phenyloxyacrylate.* The chlorohydrin was treated with excess of alcoholic sodium hydroxide, and the precipitated sodium phenyloxyacrylate separated from sodium chloride by recrystallisation from aqueous alcohol, which deposited lustrous, colourless needles. The salt was shaken with excess of concentrated ammonia and set aside during 2 weeks, after which the solution

was treated as in the foregoing cases. The m. p. (230—232°) was not depressed by admixture with the previous preparations.

The N-*benzoyl* derivative was prepared by shaking with benzoyl chloride (12 g.) a solution of *cis*-phenylserine (3 g.) in water (30 c.c.) containing sodium bicarbonate (15 g.) at intervals during 2 days and then heating on the water-bath during 30 minutes. The colourless benzoyl derivative precipitated by dilute hydrochloric acid was freed from benzoic acid by repeated extraction with hot petroleum, and was recrystallised from dilute alcohol; m. p. 197° (Found: N, 5·0. $C_{16}H_{15}O_4N$ requires N, 4·9%). It is soluble in aqueous sodium carbonate, and is thus distinguished from the yellow benzoyl compound arising from *trans*-phenylserine, this being insoluble in sodium hydroxide.

The O-*methyl* derivative was prepared by reducing α-triazo-β-methoxy-β-phenylpropionic acid with ammonium sulphide and proceeding as described in the case of *cis*-phenylserine itself. The product is readily soluble in water, and on rapid precipitation from a concentrated solution by absolute alcohol forms a white powder, m. p. 227—232° (decomp.). When allowed to evaporate slowly, the solutions deposit slender, colourless prisms which change to rhombic plates during 48 hours; m. p. 215—216° (Found: N, 6·2. $C_{10}H_{13}O_3N,2H_2O$ requires N, 6·1%. After 1 week in the desiccator: N, 6·8. $C_{10}H_{13}O_3N,H_2O$ requires N, 6·6%. Dried at 100°: N, 7·3. $C_{10}H_{13}O_3N$ requires N, 7·2%). The copper salt crystallises from boiling water in bluish-violet prisms.

The O-*methyl*-N-*benzoyl* derivative of *cis*-phenylserine was prepared by benzoylating the foregoing substance, and crystallises from alcohol in short, thick needles, m. p. 208° (Found: N, 4·8. $C_{17}H_{17}O_4N$ requires N, 4·7%). It dissolves in cold sodium carbonate solution.

The *ethyl ester picrate* separated on mixing the hydrochloride with picric acid (1 mol.), both previously dissolved in hot water, and crystallised from dilute alcohol in yellow needles, m. p. 170° (Found: N, 12·9. $C_{17}H_{18}O_{10}N_4$ requires N, 12·8%).

The *ethyl ester picrate* of the *O*-methyl derivative crystallises from dilute alcohol in yellow needles, m. p. 155° (Found: N, 12·6. $C_{18}H_{20}O_{10}N_4$ requires N, 12·4%).

The *amide* of *cis*-phenylserine, $C_6H_5{\cdot}CH(OH){\cdot}CH(NH_2){\cdot}CO{\cdot}NH_2$, was prepared by agitating the ethyl ester hydrochloride with concentrated ammonia until completely dissolved; crystals began to separate soon afterwards and were filtered off after 48 hours. It is readily soluble in boiling water, which, on cooling, deposits elongated, rectangular, transparent prisms, m. p. 199—200° (Found: N, 15·7. $C_9H_{12}O_2N_2$ requires N, 15·6%). The amide is soluble in alcohol and

is stable towards cold alkali hydroxide, in which it loses ammonia freely on boiling. Fusion is followed by liberation of ammonia and results in a yellow, alcohol-soluble resin; but it was not found possible to isolate a crystalline diketopiperazine from this.

Condensation of Glycine with Benzaldehyde.—For comparison with the new acid, *trans*-phenylserine (Erlenmeyer's) was prepared by condensing glycine with benzaldehyde. By heating these two substances at 130°, Curtius and Lederer (*Ber.*, 1886, **19**, 2462) had obtained benzylamine by an intramolecular change of the initial product, but attempts to effect combination in alcoholic solution have been uniformly unsuccessful. Erlenmeyer found, however, that in presence of sodium hydroxide the condensation proceeds rapidly, yielding

$$C_6H_5\cdot CH(OH)\cdot \underset{\displaystyle N:CH\cdot C_6H_5}{\overset{\displaystyle |}{CH}}\cdot CO_2Na \quad \text{and} \quad C_6H_5\cdot CH(OH)\cdot \underset{\displaystyle N:CH\cdot C_6H_5}{\overset{\displaystyle |}{CH}}\cdot C_6H_5;$$

both compounds lose benzaldehyde when treated with acetic acid, the products being *trans*-phenylserine and diphenylhydroxyethylamine, respectively.

On first attempting to prepare phenylserine by Erlenmeyer's method we repeatedly failed, the product being uniformly the latter of the above two substances. The reason for this was then found to be the fact that if sodium hydroxide is present in a hot, alcoholic suspension of the former substance this passes at varying speeds into the latter. This observation was made also by Erlenmeyer, who gives an explanation (*Annalen*, 1899, **307**, 117) based on (*a*) disruption of the benzylidenephenylserine molecule into benzaldehyde and benzylideneglycine, (*b*) molecular rearrangement of the latter, (*c*) re-condensation of the resulting Schiff's base, $C_6H_5\cdot CH_2\cdot N:CH\cdot CO_2Na$, with benzaldehyde and (*d*) removal of sodium glyoxylate. The following alternative explanation, however, has the advantage of simplicity:

$$CHPh(OH)\cdot CH(CO_2H)\cdot N:CHPh \longrightarrow CO_2 + CHPh(OH)\cdot CH_2\cdot N:CHPh$$
$$\longrightarrow CHPh(OH)\cdot CHPh\cdot N:CH_2 \longrightarrow CH_2O + CHPh(OH)\cdot CHPh\cdot NH_2.$$

As described by Erlenmeyer, the method makes no provision for this occurrence, and we have modified it accordingly as follows: Glycine (3·7 g.) dissolved in water (20 c.c.) was mixed with alcohol (10 c.c.) and benzaldehyde (10·6 g.); sodium hydroxide (7 g. of 94%) dissolved in water (20 c.c.) was added, the emulsion being cooled and shaken during 5 minutes; it then became clear and solid particles began to separate. After about ½ hour, the liquid had changed to a paste, which augmented in density during 24 hours; the solid was then filtered off, and this product, instead of being extracted with boiling alcohol as recommended by Erlenmeyer, was

first freed from sodium hydroxide by repeated treatment with cold alcohol, followed each time by filtration with the aid of the pump. The residue was then allowed to become dry in air, extracted with hot water, and filtered from the benzylidene derivative of diphenylhydroxyethylamine. The sodium salt of benzylidenephenylserine separated from the filtrate, which was turbid, owing to liberation of some benzaldehyde; acetic acid was therefore added, followed by two extractions with ether, and the liquid, thus freed from benzaldehyde, was evaporated to small bulk. Phenylserine (5·5 to 6·0 g.) separated over-night in lustrous, hexagonal laminæ, and was recrystallised either by rapidly cooling a hot, concentrated aqueous solution, or by adding absolute alcohol to a cold, concentrated aqueous solution. Thus purified, *trans*-phenylserine has m. p. 200—202° (decomp.).

From this material, by the action of hot acetic anhydride, we obtained the acetylaminocinnamic acid lactimide mentioned by Erlenmeyer; it crystallises in pale yellow, silky needles with m. p. 148°. *cis*-Phenylserine, however, when heated with acetic anhydride does not give the lactimide. Furthermore, on benzoylation in sodium carbonate solution, *trans*-phenylserine gave the benzoylaminocinnamic acid lactimide crystallising in pale yellow, silky needles having m. p. 164°, unaffected by admixture with the product of condensing hippuric acid and benzaldehyde in hot acetic anhydride and sodium acetate. In this process of benzoylation there was formed a very small proportion of a colourless substance melting at 160°, when it decomposes to a yellow resin, but the quantity was too small for a decision on the question whether *trans*-phenylserine yields a genuine benzoyl derivative.

Both lactimides are insoluble in cold aqueous sodium hydroxide. A recent paper by Bettzieche (*Z. physiol. Chem.*, 1925, **150**, 177) adds the *p*-toluenesulphonyl derivative and mentions various properties of Erlenmeyer's phenylserine without noticing the difficulty in preparation observed above, although the conversion of the sodium salt of phenylserine into diphenylhydroxyethylamine is confirmed.

Attempts to prepare the Diketopiperazine.—The product of heating *cis*-phenylserine for varying periods over a wide range of temperature was an amber-like resin freely soluble in alcohol. We have uniformly failed to obtain a crystalline substance from it, and also by heating *cis*-phenylserine or its *O*-methyl derivative with anhydrous oxalic acid, hydrogen potassium sulphate and phosphorus trichloride. Heating with glycerol and zinc chloride gave benzaldehyde. Similar experiments with the ester hydrochlorides and picrates were equally unfruitful.

These results are the more disappointing because, although the readiness with which picrorocellin loses water and methyl alcohol diminishes the likelihood of producing the parent diketopiperazine of which picrorocellin is the *ON*-dimethyl derivative, it was reasonable to expect from one or more of the foregoing materials a smooth transformation into 2 : 5-diketo-3 : 6-dibenzylidenepiperazine, of which xanthorocellin is the *N*-methyl derivative and is very sparingly soluble in alcohol.

Even on heating picrorocellin itself, however, when passage to xanthorocellin takes place in two stages (Forster and Saville, *loc. cit.*), it is only the former stage, namely, loss of water, which leads easily to a crystalline product; the conversion of anhydropicrorocellin into xanthorocellin by loss of methyl alcohol leads to resinous products from which isolation of xanthorocellin is attended by considerable loss.

We therefore believe that more systematic manipulation of *cis*-phenylserine or, preferably, *trans*-phenylserine in larger quantity would make it possible to isolate the diketopiperazine, because the colour test described by Abderhalden and Komm (*Z. physiol. Chem.*, 1924, **140**, 99) has enabled us to show that it is formed. On heating *cis*-phenylserine at its melting point until decomposition appeared complete (1—2 mins.), covering the residue with a hot solution of 3 : 5-dinitrobenzoic acid in saturated aqueous sodium carbonate, and boiling the mixture (1—2 mins.), we observed the intense red coloration described by Abderhalden and Komm.

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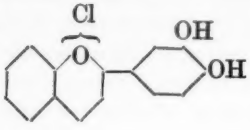
BANGALORE, S. INDIA. [*Received, May 3rd*, 1926.]

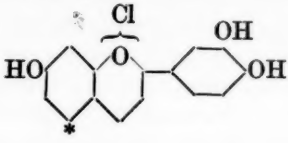
CCLIX.—*A Synthesis of Pyrylium Salts of Anthocyanidin Type. Part IX. Some Hydroxyflavylium Salts.*

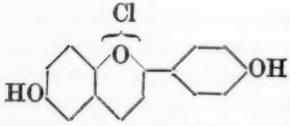
By ALEXANDER ROBERTSON and ROBERT ROBINSON.

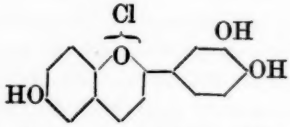
A KNOWLEDGE of the behaviour of various hydroxylated flavylium salts is of great importance as an accessory in the determination of the constitution of the anthocyanins and we have prepared new members of the group in order to confirm conclusions already drawn and to ascertain whether fresh features of interest would emerge. An intense ferric chloride reaction in this series is regarded by Willstätter as diagnostic of a free catechol grouping, the hydroxyl groups being usually in positions 3′ and 4′. We now find that the simplest conceivable flavylium salt (I) satisfying the condition

exhibits the reaction and therefore there can be no auxiliary requirements. Other 3′ : 4′-dihydroxyflavylium salts described in

(I.) 

(II.) 

(III.) 

(IV.) 

this communication develop an intense coloration with ferric chloride, whilst those not containing *o*-situated hydroxyl groups do not. Butinidin chloride (II) exhibits practically the same reactions with alkalis as luteolinidin chloride, which contains a further hydroxyl group in the asterisked position 5. This confirms the view, previously arrived at from a comparison of fisetinidin and cyanidin, that position 5 is of little value in the alkali reaction provided that position 7 is hydroxylated.

The effect of a hydroxyl group in position 6 on the alkali colour reaction of flavylium salts is remarkable. 6 : 4′-Dihydroxyflavylium chloride (III) and 6 : 3′ : 4′-trihydroxyflavylium chloride (IV) dissolve in aqueous sodium carbonate to stable crimson and purplish-blue solutions, respectively.

All the salts described in this communication are completely extracted from an aqueous acid solution by *iso*amyl alcohol.

Experimental.

2-Hydroxystyryl 3 : 4-Dimethoxyphenyl Ketone, $HO{\cdot}C_6H_4{\cdot}CH{:}CH{\cdot}CO{\cdot}C_6H_3(OMe)_2$.—A mixture of salicylaldehyde (2·4 g.), acetoveratrone (3·6 g.), potassium hydroxide (4 g.) dissolved in a little water, and methyl alcohol (200 c.c.) was boiled under reflux for 8 hours, then cooled, and acidified with dilute acetic acid. The dark orange oil precipitated by the addition of water solidified on standing; it (4·5 g.) then crystallised from methyl alcohol in glistening, orange-yellow, elongated prisms, melting at 150—151° to a dark green liquid (Found : C, 71·5; H, 5·6. $C_{17}H_{14}O_4$ requires C, 71·8; H, 5·6%).

3′ : 4′-Dimethoxyflavylium Ferrichloride.—The unsaturated ketone (4 g.) just described was converted by the action of hydrogen chloride in cold absolute formic acid solution into a pyrylium chloride, which was isolated (3·9 g.) by the addition of ether and crystallised from 2% hydrochloric acid in fine red needles. The

ferrichloride was precipitated in the usual manner as a red, amorphous mass and crystallised from acetic acid in red plates with jagged saw-like edges, exhibiting a brilliant green reflex. The salt, m. p. 196—196·5°, is moderately readily soluble in hot acetic acid (Found: C, 44·2; H, 3·4. $C_{17}H_{15}O_3Cl_4Fe$ requires C, 43·9; H, 3·2%).

3′ : 4′-*Dihydroxyflavylium Chloride* (I).—A mixture of 3′ : 4′-dimethoxyflavylium chloride (3 g.), phenol (8 g.) and hydriodic acid (60 c.c.; *d* 1·7) was gently boiled for 30 minutes in an atmosphere of carbon dioxide and on cooling, the demethylated iodide partly separated in red, prismatic needles. After the addition of water (50 c.c.) and ether (100 c.c.), the salt was collected, washed with ether, and dried (2·5 g.). The iodide was dissolved in methyl alcohol (150 c.c.) containing a trace of hydrogen chloride and converted into the *chloride* by treatment with an excess of silver chloride at the b. p. of the solvent for 15 minutes. The filtered solution, after being concentrated to half its volume, was mixed with 50 c.c. of 10% hydrochloric acid; on cooling, dark red, prismatic needles were deposited (Found in material dried in a high vacuum over sulphuric acid for 48 hours: C, 63·4; H, 4·5. $C_{15}H_{11}O_3Cl,0·5H_2O$ requires C, 63·5; H, 4·2%). The analysed specimen was hygroscopic; its alcoholic ferric chloride reaction was intense purplish-violet and its solution in aqueous sodium carbonate was violet and stable for 15 minutes. The violet coloration did not become blue on the addition of sodium hydroxide.

7-*Hydroxy*-3′ : 4′-*dimethoxyflavylium Ferrichloride*.—A slow stream of dry hydrogen chloride was led through a solution of β-resorcylaldehyde (3·45 g.) and acetoveratrone (4·25 g.) in acetic acid (20 c.c.) for 3 hours and next day the pyrylium salt was precipitated by the addition of ether (400 c.c.). It crystallised from 2% hydrochloric acid in characteristically twinning, stellate aggregates of slender, red needles (yield, 3·5 g.). The corresponding *ferrichloride* crystallised from acetic acid in dull, brick red, slender, prismatic needles, m. p. 182—183° (Found: C, 42·4; H, 3·4. $C_{17}H_{15}O_4Cl_4Fe$ requires C, 42·3; H, 3·1%).

7 : 3′ : 4′-*Trihydroxyflavylium Chloride* (*Butinidin Chloride*) (II).—7-Hydroxy-3′ : 4′-dimethoxyflavylium chloride (2·5 g.) was subjected to a demethylation process similar to that described above and, on cooling, the iodide separated in red prisms (2 g.). After this had been converted into the *chloride*, the volume of the hot methyl-alcoholic solution was reduced to 50 c.c. and 50 c.c. of 10% hydrochloric acid were added. Dark red, prismatic needles with a purple lustre separated, and these were washed and dried in a high vacuum over sulphuric acid for 48 hours (Found: C, 60·4;

H, 4·2. $C_{15}H_{11}O_4Cl,0{\cdot}5H_2O$ requires C, 60·1; H, 4·0%). The orange-red solution in alcohol becomes pink on dilution and gives a bluish-violet coloration on the addition of ferric chloride. The alkali reactions in alcoholic solution resemble those of mecocyanin in aqueous solution, that is, with sodium carbonate a fine reddish-blue is obtained and this becomes greenish-blue on the addition of sodium hydroxide. In aqueous solution, the colours, especially with sodium hydroxide, are much redder.

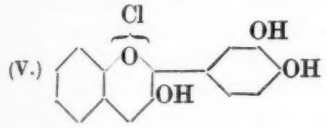
3 : 3′ : 4′-*Trimethoxyflavylium Ferrichloride*.—The condensation of salicylaldehyde and ω-methoxyacetoveratrone * (J., 1925, **127**, 170) in methyl-alcoholic solution in presence of potassium hydroxide did not proceed in a satisfactory manner, but the direct process was found to be feasible in this case.† A solution of salicylaldehyde (1·4 g.) and ω-methoxyacetoveratrone (2 g.) in acetic acid (10 c.c.) was saturated with hydrogen chloride for ½ hour, and the pyrylium salt then precipitated as a red mass by the addition of ether. The chloride is readily soluble in dilute hydrochloric acid and crystallises from 10% hydrochloric acid in very slender, long, red needles with a golden-green reflex. The *ferrichloride*, prepared in the usual way, crystallised from acetic acid in long, glistening, dark reddish-crimson prisms, m. p. 173° (Found: C, 43·7; H, 3·4. $C_{18}H_{17}O_4Cl_4Fe$ requires C, 43·6; H, 3·4%).

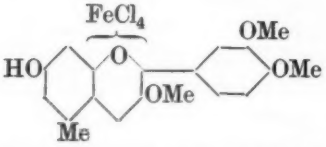
3 : 3′ : 4′-*Trihydroxyflavylium Chloride* (V).—A mixture of 3 : 3′ : 4′-trimethoxyflavylium chloride (4·5 g.), phenol (12 g.), and hydriodic acid (100 c.c.; *d* 1·7) was gently boiled (oil-bath at 130—132°) in a stream of carbon dioxide for 30 minutes. After the introduction of water (50 c.c.) the phenolic layer was separated, added to an excess of ether, and the red precipitate of the iodide collected and dried (2·5 g.). Following conversion of the iodide into the *chloride* in the usual manner in methyl-alcoholic solution, the volume of the liquid was reduced to 20 c.c. and warm concentrated hydrochloric acid (5 c.c.) and ether (100 c.c.) were successively added, the mixture being then kept in a stoppered vessel. Slender, dark brown, prismatic needles gradually separated and these were collected and dried in a high vacuum over phosphoric anhydride for 48 hours. The substance acquired a dull green reflex and was very hygroscopic (Found: C, 56·9; H, 4·8. $C_{15}H_{11}O_4Cl,1{\cdot}5H_2O$ requires C, 56·7; H, 4·4%). This salt is very readily soluble in dilute hydrochloric acid. A purplish-violet coloration is developed

* Employing ethyl methoxyacetate (150 g.) and sodium (18 g.), we obtained 90—92 g. of ethyl αγ-dimethoxyacetoacetate, b. p. 128—130°/15 mm.; and from 38 g. of the latter ester and 40 g. of veratroyl chloride, 23 g. of ω-methoxyacetoveratrone, m. p. 62°, could be isolated.

† Exceptional when salicylaldehyde is one of the components.

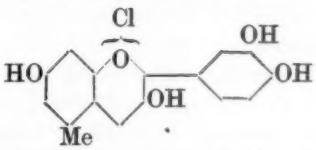
with ferric chloride in alcoholic solution, whilst sodium carbonate gives a reddish-purple coloration which quickly fades, especially in aqueous solution. The addition of sodium hydroxide to an acid aqueous solution gives almost at once a yellow liquid. The behaviour recalls that of galanginidin chloride and therefore stability to alkalis appears to be associated with the simultaneous occurrence of hydroxyl groups in both benzene nuclei of the flavylium system.





7-*Hydroxy*-3 : 3′ : 4′-*trimethoxy*-5-*methylflavylium Ferrichloride* (VI).—A stream of hydrogen chloride was passed through a solution of orcylaldehyde (2 g.) and ω-methoxyacetoveratrone (2·5 g.) in absolute formic acid (15 c.c.) for 2 hours. The chloride partly separated in fine, dark red, elongated prisms with a striking golden glance and a further quantity was precipitated by the addition of ether (yield, 3·5 g.). The salt is moderately readily soluble in hot 1% hydrochloric acid and crystallises, on cooling, in deep crimson needles which are bronze in mass; it is sparingly soluble in hot 10% hydrochloric acid. The rhodamine-pink solution in alcohol becomes crimson on the addition of sodium acetate and the aqueous solution is completely decolorised on great dilution, the colour being fully restored by the addition of hydrochloric acid. The *ferrichloride* crystallised from acetic acid in long, reddish-brown prisms, melting at 182—183° to a green liquid after softening at 178° (Found: C, 43·6; H, 4·0. $C_{19}H_{19}O_5Cl_4Fe$ requires C, 43·5; H, 3·6%). This derivative is more readily soluble in cold acetic acid than most flavylium ferrichlorides; it exhibits a golden-green streak when rubbed on a glass surface.

3 : 7 : 3′ : 4′-*Tetrahydroxy*-5-*methylflavylium Chloride*,



—In the demethylation of the chloride (2 g.) described in the last section, the usual method was employed, but the amount of phenol had to be increased (to 26 g.) in order to avoid premature separation of iodides. The bright red, prismatic needles (1·8 g.) of the iodide were collected and converted into the *chloride*, by means of silver

chloride, in ethyl-alcoholic solution (500 c.c.) containing concentrated hydrochloric acid (10 c.c.). The liquid was concentrated by distillation to about half its volume; on cooling, the chloride was deposited as a mass of slender, crimson needles with a brilliant green reflex (Found in material dried in a vacuum over sulphuric acid for 24 hours: C, 58·9; H, 4·4; and in material dried in a vacuum over phosphoric anhydride for 24 hours and then at 105° in a high vacuum for 20 minutes: C, 60·1; H, 4·4. $C_{16}H_{13}O_5Cl,0{\cdot}25H_2O$ requires C, 59·1; H, 4·2%. $C_{16}H_{13}O_5Cl$ requires C, 60·0; H, 4·1%). This salt is sparingly soluble in cold 1% hydrochloric acid and in hot 10% hydrochloric acid. It is also sparingly soluble in alcohol, giving a bluish-pink solution. Its ferric chloride reaction is similar to that of fisetinidin and cyanidin. In aqueous solution it gives a pure blue coloration with sodium carbonate or sodium hydroxide and in alcoholic solution the reaction closely resembles that of cyanidin.

6 : 4′-*Dihydroxyflavylium Chloride* (III).—6 : 4′-Dimethoxyflavylium chloride (Ridgway and Robinson, J., 1924, **125**, 221) (3 g.) was demethylated in the usual manner in presence of phenol (18 g.), and the iodide (2·8 g.) was precipitated by the addition of ether to the separated phenolic layer. Conversion into the *chloride* was accomplished in boiling 2% hydrochloric acid solution by means of silver chloride; the salt separated from the filtered solution in long, glistening, orange-red needles which were recrystallised from 2% hydrochloric acid and then dried in a high vacuum over sulphuric acid for 24 hours (Found: C, 61·8; H, 4·4. $C_{15}H_{11}O_3Cl,H_2O$ requires C, 61·5; H, 4·4%). Sodium carbonate or hydroxide added to an aqueous acid solution gives a stable, bright crimson solution. The shade is a little bluer in alcoholic solution.

6 : 3′ : 4′-*Trimethoxyflavylium Ferrichloride*.—Hydrogen chloride was passed into a mixture of 2-hydroxy-5-methoxybenzaldehyde (3·0 g.), acetoveratrone (3·6 g.), and acetic acid (20 c.c.) for 1 hour and, next day, ether (400 c.c.) was added, causing the separation of the pyrylium salt in an amorphous condition. The substance was collected, dissolved in hot 5% hydrochloric acid, and sufficient hot concentrated hydrochloric acid added to the filtered liquid to produce a 15% acid solution. On cooling, the salt crystallised in stellate aggregates of slender, red needles (6 g.). The *ferrichloride*, prepared in the usual manner, crystallised from a rapidly cooled solution in acetic acid in dull, red needles, but, by slow cooling, it could be obtained in red plates, m. p. 186°, exhibiting a bright green reflex (Found: C, 43·5; H, 3·5. $C_{18}H_{17}O_4Cl_4Fe$ requires C, 43·6; H, 3·4%).

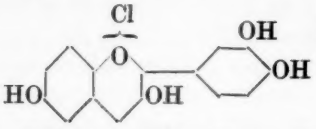
6 : 3′ : 4′-*Trihydroxyflavylium Chloride* (IV).—The chloride (2·5 g.)

last described was demethylated in the usual way in presence of phenol (2 g.), and the resulting iodide (1·5 g.) was deposited from the cooled hydriodic acid solution in stellate aggregates of bright red needles. The double decomposition with silver chloride was carried out in presence of hot 5% hydrochloric acid and after the reaction the concentration of acid in the filtered solution was doubled. Almost complete separation of the salt ensued on cooling and the substance was recrystallised in a similar manner and obtained in long, dark crimson, prismatic needles with a bluish-purple lustre (Found in material dried in a high vacuum over sulphuric acid for 24 hours: C, 58·1; H, 4·2. $C_{15}H_{11}O_4Cl,H_2O$ requires C, 58·3; H, 4·2%). Ferric chloride added to the deep red, alcoholic solution produces a purplish-violet coloration, whilst the colour of the solution in aqueous sodium carbonate is purplish-blue and stable. In presence of sodium hydroxide the blue colour is similar, but gradually becomes green and fades.

3 : 6 : 3′ : 4′-*Tetramethoxyflavylium Ferrichloride*.—The condensation of 2-hydroxy-5-methoxybenzaldehyde (2·3 g.) and ω-methoxyacetoveratrone (3 g.) was carried out like the analogous process last described; the salt precipitated by ether crystallised from 5% hydrochloric acid in very long, slender, bright red needles (5·4 g.). The *ferrichloride* is readily soluble in formic acid and sparingly soluble in acetic acid; it crystallises from a mixture of equal volumes of the two in long, shining, dark red, prismatic needles, m. p. 198—199° (Found: C, 43·6; H, 3·7. $C_{19}H_{19}O_5Cl_4Fe$ requires C, 43·5; H, 3·6%).

3 : 6 : 3′ : 4′-*Tetrahydroxyflavylium Chloride* (VII).—4·5 Grams of 3 : 6 : 3′ : 4′-tetramethoxyflavylium chloride were demethylated by hydriodic acid (150 c.c.; *d* 1·7) in presence of phenol (24 g.) as usual, and water (100 c.c.) was added to the cooled solution. The phenolic layer was separated and added to ether (500 c.c.), which caused the deposition of a mass of microscopic, red needles (2·3 g.). Conversion into the *chloride* and crystallisation of the resulting salt were accomplished in 2% and from 10% hydrochloric acid solutions, respectively, and on recrystallisation from 10% hydrochloric acid (2% increased to 10% by the addition of concentrated acid) the chloride was obtained in dark red plates exhibiting a brilliant green glance (Found in material dried in a high vacuum over phosphoric anhydride for 48 hours; C, 58·9; H, 4·0. $C_{15}H_{11}O_5Cl$ requires C, 58·7; H, 3·6%). The eosin-red, alcoholic solution gives a violet-blue coloration with ferric chloride. The solution in aqueous sodium carbonate is reddish-blue, whilst in alcoholic sodium carbonate only a permanganate-coloured solution is obtained—a quite unusual reversal of the changes commonly

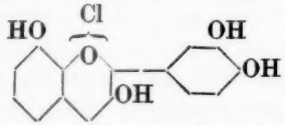
observed. Sodium hydroxide produces unstable colorations, but in alcoholic solution the reaction is pure blue.

(VII.)  (VIII.)

8 : 3′ : 4′-*Trimethoxyflavylium Ferrichloride* (VIII).—Hydrogen chloride was led for 2 hours into a cold solution of *o*-vanillin (1·7 g.) and acetoveratrone (2 g.) in formic acid (8 c.c.) and, after a few hours, the pyrylium salt was precipitated by ether and collected (3 g.). The chloride crystallised very slowly from a solution in 5% hydrochloric acid in red, prismatic needles (1·5 g.). This salt is readily soluble even in moderately concentrated hydrochloric acid, and it does not appear to be so stable as the majority of analogous substances. The *ferrichloride* crystallises from acetic acid in short, pointed, flat prisms, m. p. 193—194° (Found : C, 43·6; H, 3·4. $C_{18}H_{17}O_4Cl_4Fe$ requires C, 43·6; H, 3·4%). The derivative has a dark red colour in suspension in acetic acid, but in mass appears green on account of the brilliant reflex. All attempts to demethylate the salts of this series were fruitless, and complete decomposition occurred under the usual conditions.

3 : 8 : 3′ : 4′-*Tetramethoxyflavylium Ferrichloride*.—The condensation of *o*-vanillin and ω-methoxyacetoveratrone with the aid of hydrogen chloride was carried out in acetic acid solution, and the crude product precipitated by ether was dissolved in 2% hydrochloric acid; after the concentration of the acid had been quintupled, the chloride crystallised in long, dark crimson needles with a purple lustre. A further quantity was collected after the hydrochloric acid concentration had been brought to 15%. The total yield was good. The *ferrichloride* crystallised from acetic acid in long, glistening, dark red, prismatic needles, m. p. 162—163° (Found : C, 43·7; H, 3·8. $C_{19}H_{19}O_5Cl_4Fe$ requires C, 43·5; H, 3·6%).

3 : 8 : 3′ : 4′-*Tetrahydroxyflavylium Chloride*,



—A mixture of 3 : 8 : 3′ : 4′-tetramethoxyflavylium chloride (2 g.), phenol (14 g.), and hydriodic acid (75 c.c.; *d* 1·7) was gently boiled (bath at 130—132°) for 30 minutes in an atmosphere of carbon dioxide. After the addition of water (50 c.c.), the phenolic layer was separated and the iodide (1·0 g.) precipitated as a bright red, amorphous mass by the addition of ether (300 c.c.). The iodide

(2 g.) was dissolved in methyl alcohol (80 c.c.) containing a trace of hydrogen chloride, and the solution heated for 15 minutes after the introduction of an excess of precipitated silver chloride. The filtered liquid was concentrated to one-half its volume, 5 c.c. of concentrated hydrochloric acid were added, and the solution was concentrated to about 30 c.c. The salt then separated, on the gradual addition of ether, in aggregates of microscopic, prismatic needles. A solution of the salt in a little 5% hydrochloric acid was mixed with so much concentrated acid that the concentration was raised to 15% and, on standing 48 hours, dark red, prismatic needles were deposited and were then collected. The yield was poor and the material from several operations was combined and twice recrystallised in a similar manner (Found in material dried over phosphoric anhydride in a high vacuum for 36 hours: C, 55·2; H, 5·1; and in material dried similarly for 18 days: C, 59·0; H, 4·3. $C_{15}H_{11}O_5Cl$ requires C, 58·7; H, 3·6%. $C_{15}H_{11}O_5Cl,H_2O$ requires C, 55·4; H, 4·0%).

The high values found for the hydrogen content are undoubtedly due to the extremely hygroscopic nature of this salt. The orange-red alcoholic solution becomes purplish-violet on the addition of ferric chloride. With sodium carbonate, this isomeride of fisetinidin chloride gives an unstable purplish-red coloration, and the reaction with sodium hydroxide is similar.

We desire to thank the International Education Board of New York for a Fellowship which has enabled one of us to take part in the investigation, and the Government Grant Committee of the Royal Society for a grant which has defrayed a part of the expense of the work.

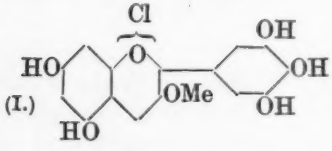
THE UNIVERSITY, MANCHESTER. [*Received, March 26th*, 1926.]

CCLX.—*A Synthesis of Pyrylium Salts of Anthocyanidin Type. Part X. Delphinidin Chloride 3-Methyl Ether.*

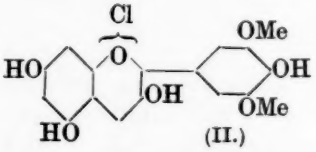
By ELISABETH STEWART GATEWOOD and ROBERT ROBINSON.

AMONG the naturally occurring methyl ethers of delphinidin a constitution can be unequivocally assigned to ampelopsidin alone. This is considered by Willstätter and Zollinger (*Annalen*, **1916**, **412**, 216) to be the 4′-methyl ether on account of the weak ferric chloride reaction. Furthermore, since neither myrtillidin nor petunidin gives rise to a methylated phloroglucinol fragment even

on treatment with concentrated alkalis at relatively low temperatures, Willstätter and his collaborators concluded that each of these monomethyl ethers of delphinidin possessed free hydroxyl groups in positions 5, 7, and 4′. Apparently, therefore, one of these anthocyanidins should be delphinidin 3-methyl ether and the other the 3′-methyl ether. We have synthesised a flavylium salt which is regarded (see below) as delphinidin chloride 3-methyl ether (I), but it is quite different from myrtillidin chloride and from petunidin chloride. The new salt is, for example, very much more sparingly soluble in dilute hydrochloric acid than are the isomerides originating from natural sources.* Probably, therefore, one of the salts—myrtillidin chloride or petunidin chloride—is pure delphinidin chloride 3′-methyl ether and the other is either the same substance in a less pure condition,† or, after all, has a methoxyl group in position 5 or 7 in the phloroglucinol nucleus. And, further, since myrtillidin is derived from two distinct anthocyanins whilst definite evidence was obtained that petunidin has a methoxyl group outside the phloroglucinol nucleus, therefore, in connexion with the above alternatives, it would be petunidin which might be less pure myrtillidin or myrtillidin which has a methoxyl in the phloroglucinol nucleus.



(I.)



(II.)

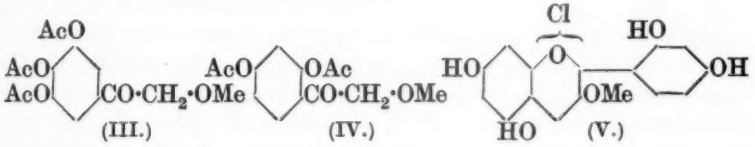
We take this opportunity of pointing out that the bearing of the evidence for the constitution of malvidin chloride is not free from ambiguity. Willstätter and Mieg (*Annalen*, 1915, **408**, 122) consider that one of the methoxyl groups is in the phloroglucinol nucleus, and this being so, the remaining methoxyl must be in position 4′, since the ferric chloride reaction is weak. But this leaves two of the three free phenolic hydroxyls of malvin in positions which do not contribute to strong alkali colour reaction, and yet malvin dissolves in aqueous sodium carbonate to a blue solution. It seems better to regard malvidin provisionally as delphinidin 3′ : 5′-dimethyl ether—a dimethoxypelargonidin (II)—and this formulation is the only one in harmony with the colour reactions. The methoxylated phenolic compound obtained on fusion with

* We are greatly indebted to Geheimrath Prof. R. Willstätter for a specimen of myrtillin chloride.

† Myrtillidin and petunidin have identical reactions but differ in crystalline form and in some solubility relations.

alkali would then be a pyrogallol derivative.* An attempt to synthesise delphinidin 3′ : 5′-dimethyl ether is in progress.

The course of the synthesis of delphinidin chloride 3-methyl ether did not run smoothly and it is necessary at this stage to consider carefully the evidence bearing on the constitution of the product. Triacetylgalloyl chloride was allowed to react with ethyl (or methyl) sodio-$\alpha\gamma$-dimethoxyacetoacetate in ethereal solution, and the product hydrolysed by means of dilute aqueous alcoholic potassium hydroxide on the steam-bath. After acidification the solution was extracted with ether and then with butyl alcohol. The product from the ether extract, on acetylation with acetyl chloride, afforded a crystalline substance, m. p. 132—133°, which gave results on analysis in close agreement with those required for a triacetoxy-ω-methoxyacetophenone (III). Since the methoxyl content and molecular weight were also found to be in harmony with this hypothesis, it is extremely difficult to suggest an alternative interpretation and we therefore designate the substance in accordance with this view. The anomaly arises from the circumstance that this crystalline compound exhibits no tendency to condense with 2 : 4 : 6-triacetoxybenzaldehyde, β-resorcylaldehyde or *o*-vanillin in formic acid solution in the presence of hydrogen chloride to give flavylium salts. For comparison we prepared 2 : 4-diacetoxy-ω-methoxyacetophenone (IV) by acetylation of ω-methoxyresacetophenone (Slater and Stephen, J., 1920, **117**, 312) and experienced little difficulty in condensing this substance with 2 : 4 : 6-triacetoxybenzaldehyde, ultimately obtaining *morinidin chloride 3-methyl ether* (V).

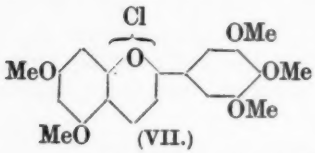


The butyl-alcoholic extract, to which reference has already been made, yielded no crystalline material, but the acetylated product condensed under the usual conditions with 2 : 4 : 6-triacetoxybenzaldehyde and after hydrolysis our delphinidin chloride 3-methyl ether (I) was obtained. The only explanation of these observations which has occurred to us is that the hydrolysis of the original condensation product, $(OAc)_3C_6H_2\cdot CO\cdot C(OMe)(CO_2Et)\cdot CO\cdot CH_2\cdot OMe$, was incomplete and that whilst ether extracted the trihydroxy-

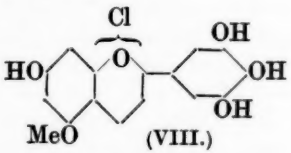
* This would be more readily produced from a *p*-hydroxybenzoic acid than from a *p*-methoxybenzoic acid, that is, more readily from malvidin than from oenidin on the suggested hypothesis.

ω-methoxyacetophenone, the triacetyl derivative of which is not reactive, butyl alcohol also extracted a compound containing the group $(HO)_3C_6H_2{\cdot}CO{\cdot}CH(OMe){\cdot}COR$. After acetylation, the latter substance reacted with the benzaldehyde derivative with simultaneous expulsion of the group –COR. Apart from the method of synthesis, the examination of the new delphinidin methyl ether, details of which will be found in the experimental section, leaves little room for doubt in regard to its constitution. The alkali colour reaction of the salt is much redder than that of delphinidin and the alteration is similar to that which occurs on passing from cyanidin to luteolinidin or from cyanin to mecocyanin.

For comparison, we wished to synthesise 5 : 7 : 3′ : 4′ : 5′-pentahydroxyflavylium chloride and accordingly condensed 2-hydroxy-4 : 6-dimethoxybenzaldehyde with 3 : 4 : 5-trimethoxyacetophenone to 3 : 4 : 5-*trimethoxyphenyl* 2-*hydroxy*-4 : 6-*dimethoxystyryl ketone*, $(MeO)_2C_6H_2(OH){\cdot}CH{:}CH{\cdot}CO{\cdot}C_6H_2(OMe)_3$ (VI), in the usual manner. This unsaturated ketone is converted by hydrochloric acid with great facility into 5 : 7 : 3′ : 4′ : 5′-*pentamethoxyflavylium chloride* (VII). On demethylating this and converting the product into the chloride a *tetrahydroxymethoxyflavylium chloride* was obtained which we consider to have the formula (VIII), although position 7 is an alternative situation for the methoxyl group.



(VII.)



(VIII.)

Since fisetinidin and butinidin exhibit almost the same alkali colour reactions as cyanidin and luteolinidin, respectively, (VIII) represents a salt which would doubtless closely resemble the parent pentahydroxy-derivative. It is therefore of interest that the reactions of our new tetrahydroxymethoxyflavylium chloride resemble those of the supposed delphinidin chloride 3-methyl ether. It appears to be a general rule in the series of flavylium salts containing free hydroxyl groups in positions 7, 3′, and 4′, and including cyanidin and delphinidin derivatives, that, if a violet solution of the salt in aqueous sodium carbonate becomes greenish-blue on the addition of sodium hydroxide, there is no free hydroxyl group in position 3.

Experimental.

Morinidin Chloride 3-Methyl Ether (V).—ω-Methoxyresacetophenone (Slater and Stephen, *loc. cit.*) often crystallises with water

of crystallisation and then melts unsharply at 85°. After drying over phosphoric anhydride, such specimens melt at 136—137°.

A mixture of the ketone (5 g.) and acetyl chloride (25 c.c.) was kept for 20 minutes and then gently warmed until a clear solution resulted. This was kept in a vacuum for a long time, and the oil obtained together with 2 : 4 : 6-triacetoxybenzaldehyde (5·2 g.) was dissolved in formic acid (30 c.c.) and the solution saturated with hydrogen chloride during 4 hours. On the following day the product was precipitated by the addition of ether (500 c.c.) and dissolved, after the liquid had been decanted, in ethyl alcohol (100 c.c.). Concentrated hydrochloric acid (20 c.c.) having been added, the solution was refluxed for 35 minutes; most of the alcohol was then distilled off, water (50 c.c.) added, the precipitate isolated, and extracted with boiling 0·5% hydrochloric acid (300 c.c.). The concentration of acid in the filtered extract was increased to 5%; crimson, microscopic needles (3 g.) then separated on cooling. These were recrystallised by the slow evaporation of an alcoholic solution to which so much concentrated hydrochloric acid had been added that the concentration of hydrogen chloride was 5%. The bright red needles thus obtained were dried to constant weight in a vacuum over sulphuric acid (Found: C, 56·8, 56·8; H, 3·9, 4·0; MeO, 9·1. $C_{16}H_{13}O_6Cl$ requires C, 57·1; H, 3·9; MeO, 9·2%).

The dry salt is hygroscopic; it darkens above 200°, but does not melt at 290°. On treatment with water pseudo-base formation was slow, and the colour was completely restored by the addition of hydrochloric acid (distinction from morinidin). The substance is very sparingly soluble in boiling 10% hydrochloric acid. The alcoholic solution has a deep red colour a shade yellower than that of morinidin chloride and distinctly bluer than the aqueous acid solutions. Sodium carbonate added to the latter gives a violet-red coloration, whilst sodium hydroxide produces a very unstable violet. The characteristic behaviour of morinidin on reduction is not exhibited by this monomethyl ether of the substance. On demethylation in the usual manner morinidin iodide and then morinidin chloride were obtained; these were recognised by comparison with authentic specimens. The demethylated salt gave an ether-soluble reduction product which developed an intense blue colour on solution in cold aqueous sodium hydroxide.

3 : 4 : 5-*Trimethoxyphenyl* 2-*Hydroxy*-4 : 6-*dimethoxystyryl Ketone* (VI).—3 : 4 : 5-Trimethoxyacetophenone prepared by Mauthner's method (*J. pr. Chem.*, 1910, **82**, 278) crystallised from light petroleum in needles, m. p. 76—77° (Mauthner gives m. p. 72°). The *p*-nitrophenylhydrazone, m. p. 194—195°, crystallises in bright

yellow needles (Mauthner; reddish-brown needles). The orange-red solution obtained on adding aqueous sodium hydroxide (9 g. in 13 c.c.) to a mixture of 2-hydroxy-4 : 6-dimethoxybenzaldehyde (5 g.), 3 : 4 : 5-trimethoxyacetophenone (6 g.), and methyl alcohol (25 c.c.) was kept at about 60° for 2 days, then cooled, acidified with dilute acetic acid, and the yellow solid resulting from the slow crystallisation of the viscous mass was collected, washed, and dried (yield, 10 g.). The substance crystallised from ethyl alcohol in bright yellow, blunt prisms, m. p. 151—152°, to a dark red liquid (Found: C, 64·1; H, 5·9. $C_{20}H_{22}O_7$ requires C, 64·2; H, 5·9%). The potassium salt is sparingly soluble in dilute aqueous potassium hydroxide and crystallises from the orange-yellow solution in glistening, orange needles.

5 : 7 : 3′ : 4′ : 5′-*Pentamethoxyflavylium Chloride* (VII).—The chalkone is very sensitive to acids and is changed to the flavylium salt with great facility. Actually a hot mixture of acetic acid and concentrated hydrochloric acid was employed and, on cooling, the *chloride* separated in woolly, red needles, m. p. 150°, to a beetle-green liquid. A specimen was crystallised from a mixture of methyl alcohol and hydrochloric acid and dried in a vacuum over sodium hydroxide [Found: MeO (by Pregl–Zeisel method), 31·5. $C_{15}H_6O(OMe)_5Cl$ requires 4MeO, 31·6%]. This salt is moderately readily soluble in water to a brownish-orange solution and is sparingly soluble in dilute hydrochloric acid. The corresponding base is a relatively strong one and the acetate and hydrogen carbonate are stable in cold aqueous solution. In order to prepare solutions of these salts the mauve pseudo-base, obtained by the addition of an excess of sodium carbonate to the flavylium chloride, was dissolved as far as possible in ether, and the extract shaken with dilute acetic acid or treated with water and carbon dioxide. When perchloric acid is added to an aqueous solution of the chloride a gelatinous precipitate is obtained and, on boiling, this very sparingly soluble, brick red *perchlorate* becomes crystalline in the form of microscopic, fibrous needles. The *ferrichloride* crystallises from acetic acid in slender, silky, crimson needles, m. p. 199—201° (Found: C, 43·1; H, 3·8. $C_{20}H_{21}O_6Cl_4Fe$ requires C, 43·3; H, 3·8%). The *mercurichloride* is insoluble in boiling dilute hydrochloric acid containing mercuric chloride.

7(or 5) : 3′ : 4′ : 5′-*Tetrahydroxy*-5(or 7)-*methoxyflavylium Chloride* (VIII or alternative).—A mixture of the pentamethoxyflavylium chloride (2 g.), phenol (10 g.), and hydriodic acid (100 c.c.; *d* 1·7) was boiled in an atmosphere of carbon dioxide for 30 minutes. The iodide crystallised, on cooling, in reddish-brown needles with a greenish-golden reflex (2 g.). The salt was placed in a silvered

flask along with hot alcohol (40 c.c.), concentrated hydrochloric acid (15 drops), and an excess of precipitated silver chloride. A considerable amount of the *chloride* crystallised from the hot solution and the substance (1 g.) was separated from the silver salt by extraction with boiling alcohol and addition of hydrochloric acid to the filtrates. The substance was recrystallised, by slow evaporation of an aqueous methyl-alcoholic hydrochloric acid solution, in short, flat, red needles or plates which blackened above 200° without melting (Found in material dried in a vacuum over sodium hydroxide: C, 54·2; H, 4·4. $C_{16}H_{13}O_6Cl,H_2O$ requires C, 54·3; H, 4·3%). The presence of a methoxyl group in this substance was qualitatively demonstrated by means of the Pregl–Zeisel apparatus, with a mixture of hydriodic acid, phenol and acetic anhydride as reagent. The salt is very sparingly soluble in dilute hydrochloric acid and moderately readily soluble in alcohol to a red solution which becomes blue on the addition of ferric chloride. The colorations developed in aqueous sodium carbonate and sodium hydroxide solutions are rich violet and blue, respectively.

3 : 4 : 5-*Triacetoxy*-ω-*methoxyacetophenone* (III).—A suspension and solution of 3 : 4 : 5-triacetoxybenzoyl chloride (30 g.; Fischer, Bergmann, and Lipschutz, *Ber.*, 1918, **51**, 45) in dry ether was gradually added to the product of the action of granulated sodium (2·2 g.) on an ethereal solution of methyl αγ-dimethoxyacetoacetate (18 g.; Pratt and Robinson, J., 1925, **127**, 168). The mixture was boiled for 2 hours, kept over-night, and again boiled for 2 hours. After removal of the ether by distillation, the residue was quickly added to a mixture of alcohol (500 c.c.) and aqueous potassium hydroxide (1000 c.c. of 2·5%) through which hydrogen had been led, and agitation by means of a stream of the gas was continued for several hours. After 12 hours the solution was refluxed in an atmosphere of hydrogen for 4 hours, then cooled, acidified with dilute hydrochloric acid, and concentrated to a small volume under diminished pressure. The liquid was twice extracted with ether and then with warm butyl alcohol. The material left after removal of the solvent from the dried (sodium sulphate) ethereal extract partly solidified (2·8 g.) and was acetylated by heating it for 15 minutes with acetyl chloride. The excess of the reagent was distilled away in a vacuum, and the solution of the crude product in acetone shaken with precipitated barium carbonate and filtered. On concentration, crystals separated, and these, after being washed with ether, crystallised from alcohol (yield, 2·2 g.) in colourless, rhombic tablets, m. p. 132—133° (Found: C, 55·4, 55·4; H, 4·7, 4·8; MeO, 9·6; *M*, cryoscopic in camphor, 327. $C_{14}H_{13}O_7{\cdot}OMe$ requires C, 55·5; H, 5·0; MeO, 9·6%; *M*, 324). The sharp

analytical results in conjunction with the method of preparation appear to require that this substance should be regarded as 3 : 4 : 5-triacetoxy-ω-methoxyacetophenone. It is insoluble in cold dilute aqueous sodium hydroxide and gives no coloration with ferric chloride in alcoholic solution. On hydrolysis a pyrogallol derivative was produced and recognised by colour reactions.

The butyl-alcoholic extract mentioned above was dried with sodium sulphate and the solvent removed by distillation in a vacuum, leaving a dark oil (12 g.) from which no crystalline product could be isolated. This material was acetylated exactly like the product from the ethereal extract, and treatment with barium carbonate in acetone solution was again practised. The acetylated product was a dark oil (A) and did not crystallise.

5 : 7 : 3′ : 4′ : 5′-*Pentahydroxy*-3-*methoxyflavylium Chloride* (I).—A stream of hydrogen chloride was passed through a solution of 2 : 4 : 6-triacetoxybenzaldehyde (5 g.) and the oil (A) (10 g.) in anhydrous formic acid (30 c.c.) for 4 hours. After 12 hours, the solid precipitated by the addition of ether was hydrolysed, as in similar cases (compare Pratt and Robinson, J., 1925, **127**, 1182), by boiling aqueous-alcoholic hydrochloric acid. Most of the alcohol was removed by distillation and on the addition of water a dark reddish-brown precipitate was obtained. This was extracted several times with boiling 0·5% hydrochloric acid, the salt being recovered from the combined filtrates by the addition of concentrated hydrochloric acid. The material (1·1 g.) had a golden reflex, but was not definitely crystalline. It dissolved in hot methyl alcohol, but quickly separated again in dark brown needles and these were recrystallised by solution in boiling 0·05% hydrochloric acid and addition of a few drops of concentrated hydrochloric acid to the filtrate. Under the microscope, the crystals are seen to be very short, slender, opaque needles which usually form highly characteristic, stellate clusters. In mass the substance is deep chocolate-brown with a green reflex, especially when rubbed on paper (Found in air-dried material: C, 49·5, 49·6; H, 4·6, 4·5; Cl, 9·1, 9·0; MeO,* 7·8. $C_{15}H_{10}O_6Cl\cdot OMe,2H_2O$ requires C, 49·4; H, 4·4; Cl, 9·1; MeO, 8·0%).

The most striking property of this salt is its sparing solubility

* In the Pregl–Herzig–Meyer apparatus—earlier determinations by means of the Pregl–Zeisel apparatus and method gave low results (*e.g.*, MeO, 5·2% even in presence of phenol and acetic anhydride and on boiling for 1·5 hours). Similar results were obtained in the cases of other methoxylated pyrylium salts. Thus 7-methoxy-2 : 4-diphenylbenzopyrylium ferrichloride gave negative or very low results by the Pregl–Zeisel method and approximately correct results when the Pregl–Herzig–Meyer apparatus was employed. This behaviour is, however, exceptional.

in aqueous hydrochloric acid. It is practically insoluble in cold 0·1% hydrochloric acid and very sparingly soluble in boiling 1% acid. The solution in hot 0·05% hydrochloric acid is more brownish-red than that of delphinidin. The salt is soluble in alcohol to a rich bluish-crimson solution and on the addition of ferric chloride this becomes pure blue. The solution in aqueous sodium carbonate is bluish-violet and becomes pure blue on the addition of sodium hydroxide. (The colorations are more or less rapidly destroyed as the result of aërial oxidation.) The formation of a colourless pseudo-base and of a deep violet colour-base was observed under the usual conditions and the salt is completely extracted from aqueous solutions by *iso*amyl alcohol. Owing to the insolubility of the iodide, great difficulty was experienced in the demethylation of the salt. A mixture of the chloride (2 g.), phenol (35 g.), and hydriodic acid (65 c.c.; *d* 1·7) was boiled in an atmosphere of carbon dioxide for 3 hours, but a clear solution was not produced at any stage. Unchanged iodide (0·91 g.) was collected on a sintered-glass filter, and crude delphinidin iodide (0·45 g.) separated from the mother-liquor on standing. The recovered unchanged iodide (0·91 g.) was boiled with phenol (50 g.) and hydriodic acid (50 c.c.) for 1 hour, but again 0·56 g. was recovered and the delphinidin iodide obtained amounted to 0·08 g. A further quantity of the original chloride was dissolved in phenol on the steam-bath, and hydriodic acid (*d* 1·96) gradually added to the solution boiling in an atmosphere of carbon dioxide. Even in this case the iodide of the methoxylated base separated. The delphinidin iodide was recrystallised from phenol–hydriodic acid and then converted in the usual manner into the crystallised chloride. This material had the properties of delphinidin chloride and dissolved in aqueous sodium carbonate to a pure blue solution. No differences from delphinidin chloride could be detected, but the small amount available precluded a detailed examination of the characteristic hydrates.

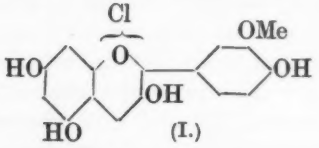
We wish to thank the Royal Society for a grant which defrayed a part of the expense of the investigation.

THE UNIVERSITY, MANCHESTER. [*Received, May 11th,* 1926.]

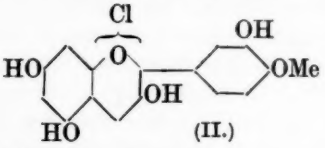
CCLXI.—*A Synthesis of Pyrylium Salts of Anthocyanidin Type. Part XI. A Synthesis of Peonidin Chloride.*

By Thomas Joseph Nolan, David Doig Pratt, and Robert Robinson.

Willstätter and Nolan (*Annalen*, 1915, **408**, 136) showed that peonin, the anthocyanin of the deep violet-red peony, yields, on hydrolysis with hydrochloric acid, glucose (2 mols.) and the anthocyanidin, peonidin chloride, $C_{16}H_{13}O_6Cl$, a monomethyl ether of cyanidin chloride. Furthermore, since the ferric chloride reaction was found to be very weak, it was suggested that the methoxy-group must be in one of the positions 3′ and 4′ in accordance with the expressions (I) and (II), of which the former was preferred.

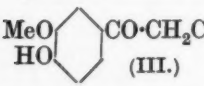


(I.)

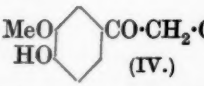


(II.)

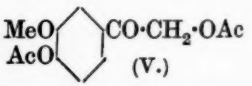
A strong argument in favour of this view can now be advanced in connexion with the circumstance that peonidin dissolves in aqueous sodium carbonate to a pure blue solution. (I) is a methoxypelargonidin chloride, whilst (II) is a methoxy-derivative of the recently synthesised 3 : 5 : 7 : 3′-tetrahydroxyflavylium chloride (J., 1925, **127**, 1186); and since the alkali colour reaction of peonidin closely resembles that of pelargonidin and differs markedly from that of the *iso*pelargonidin, the selection of the formula (I) is justified. An analogous constitution has been assigned to the flavonol, *iso*rhamnetin, and in respect of both the anthocyanidin and the anthoxanthin the correctness of these conclusions has now been confirmed by synthesis. In an earlier paper (J., 1923, **123**, 753) it was shown that the condensation of veratrole and chloroacetyl chloride in presence of aluminium chloride under suitable conditions affords ω-chloroacetovanillone (III), which may be reduced to acetovanillone.



(III.)



(IV.)



(V.)

The chloro-ketone yields the *acetoxy*-derivative (IV) on treatment with alcoholic potassium acetate, and the *diacetyl* derivative (V) is produced by subsequent acetylation. Both (IV) and (V) condense with 2 : 4 : 6-triacetoxybenzaldehyde in formic acid solution

in presence of hydrogen chloride, yielding products which give peonidin chloride on hydrolysis. The yield of the completely purified salt was small and in the synthesis of pelargonidin chloride by a similar method even greater difficulties were experienced.

EXPERIMENTAL.

ω-Acetoxy-4-hydroxyacetophenone, $HO{\cdot}C_6H_4{\cdot}CO{\cdot}CH_2{\cdot}OAc$.—A solution of ω-chloro-4-acetoxyacetophenone (30 g.) (Tutin, Caton, and Hann, J., 1909, **95**, 2119) and potassium acetate (20 g.) in alcohol (250 c.c.) was boiled for 4 hours, then filtered and concentrated by distillation of most of the alcohol. The oil precipitated by the addition of water to the residue was isolated by ether and solidified to a yellow mass (26 g.). The substance crystallises from benzene as a colourless crust, m. p. 127° (Found: C, 61·5; H, 5·2. $C_{10}H_{10}O_4$ requires C, 61·8; H, 5·1%). It is soluble in aqueous sodium carbonate but not in the bicarbonate. The 4-acetoxy-group suffers hydrolysis in the above-described process.

ω : 4-Diacetoxyacetophenone, $AcO{\cdot}C_6H_4{\cdot}CO{\cdot}CH_2{\cdot}OAc$.—This compound crystallised from light petroleum in colourless needles, m. p. 98° (Found: C, 61·0; H, 5·2. $C_{12}H_{12}O_5$ requires C, 61·0; H, 5·1%), and was prepared from the foregoing phenol by the action of cold acetyl chloride during several hours. It is insoluble in aqueous sodium carbonate.

Pelargonidin Chloride, $(HO)_2C_6H_2{\cdot}C_3HO(OH){\cdot}C_6H_4{\cdot}OH\}Cl$.—A solution of ω : 4-diacetoxyacetophenone (6·0 g.) and 2 : 4 : 6-triacetoxybenzaldehyde (7·2 g.) in absolute formic acid (30 c.c.) was saturated with hydrogen chloride during 6 hours and then kept for 2 days. The solid precipitated by the addition of much ether was collected, dissolved in alcohol (200 c.c.), and after the addition of concentrated hydrochloric acid (20 c.c.) the solution was boiled for an hour, concentrated in a vacuum to a small bulk, and the precipitate collected. The flavylium salt was purified by repeated solution in boiling 0·5% hydrochloric acid and precipitation with concentrated acid and then by crystallisation from 1% hydrochloric acid and by evaporation of an alcoholic solution to which some 10% hydrochloric acid had been added. The substance was then crystallised as iodide from a mixture of phenol and hydriodic acid, reconverted in the usual manner into chloride, and finally crystallised from aqueous alcoholic hydrochloric acid. The products from two experiments were combined and ultimately about 0·05 g. of pure pelargonidin chloride exhibiting the correct crystalline form and reactions was isolated (Found: C, 55·9; H, 4·2; Cl, 10·7. Calc. for $C_{15}H_{11}O_5Cl,H_2O$: C, 55·6; H, 4·0; Cl, 10·9%). Improvements in this direct synthesis of pelargonidin are still being sought.

ω-Acetoxy-3-methoxy-4-hydroxyacetophenone (IV).—ω-Chloroacetovanillone (20 g.), potassium acetate (15 g.), and alcohol (200 c.c.) were employed in the preparation of this substance under conditions identical with those described above. A solution of the crude product (15 g.) in a mixture of benzene and light petroleum very slowly deposited large, colourless prisms, m. p. 110° (Found: C, 59·1; H, 5·3. $C_{11}H_{12}O_5$ requires C, 58·9; H, 5·3%). The substance is readily soluble in aqueous sodium carbonate and in most organic solvents.

ω : 4-*Diacetoxy-3-methoxyacetophenone* (V).—The phenol last described was acetylated by means of acetyl chloride; the product crystallised from light petroleum in clusters of colourless needles, m. p. 73° (Found: C, 58·5; H, 5·4. $C_{13}H_{14}O_6$ requires C, 58·6; H, 5·3%). The substance is insoluble in aqueous sodium carbonate.

Peonidin Chloride (I).—(A) A solution of ω-acetoxy-3-methoxy-4-hydroxyacetophenone (5 g.) and 2 : 4 : 6-triacetoxybenzaldehyde (8·0 g.) in absolute formic acid (35 c.c.) was saturated with hydrogen chloride for 3 hours, being meanwhile cooled in running water. On the following day ether was added and the hygroscopic, crimson precipitate collected and boiled with a mixture of alcohol (150 c.c.) and concentrated hydrochloric acid (30 c.c.) for 10 minutes. Most of the alcohol was then evaporated, water (250 c.c.) added to the residue, and the mixture boiled and filtered. The deep bluish-red solution now became dichroic (bluish-red) on the addition of sodium carbonate, whereas peonidin develops a pure blue coloration. Attempts to induce the direct crystallisation of the anthocyanidin chloride were fruitless. The liquid was gently heated and picric acid (5 g.) introduced with stirring. The picrate, at first amorphous, soon crystallised in brownish-crimson leaflets and after cooling and standing for 12 hours was collected along with some picric acid.

(B) ω : 4-Diacetoxy-3-methoxyacetophenone (7 g.) was condensed with 2 : 4 : 6-triacetoxybenzaldehyde (7·5 g.) in a similar manner, except that the crude product was collected after the hydrolysis, extracted with boiling 0·5% hydrochloric acid (150 c.c.), and 10% hydrochloric acid (30 c.c.) added to the filtered solution. The whole was kept for 3 days in the ice-chest, and the brown, semi-crystalline material was then collected and dissolved in 0·5% hydrochloric acid (35 c.c.). No crystallisation occurred on keeping, but an amorphous film separated and was removed. Aqueous picric acid was added until the solution was almost decolorised, and the picrate was collected.

The picrates from (A) and (B) exhibited the same properties and

the subsequent procedure was identical in each case, the resulting peonidin chlorides being ultimately combined. The picrate separated from methyl alcohol in dark brownish-crimson, glistening, microscopic needles. The crystallised material was dissolved in methyl alcohol containing hydrogen chloride, and the chloride precipitated by ether in a flocculent condition. This process was repeated and the salt was then crystallised several times from dilute hydrochloric acid (at first 2% and later 1%), separating in chocolate needles which, air-dried, lost 4·9% in a vacuum over phosphoric anhydride (Found: C, 57·2; H, 3·9; MeO, 8·9. $C_{16}H_{13}O_6Cl,H_2O$ requires H_2O, 5·1%. $C_{16}H_{13}O_6Cl$ requires C, 57·1; H, 3·9; MeO, 9·2%). Willstätter and Nolan (*loc. cit.*) showed that peonidin chloride crystallises with $1H_2O$ which is lost in a vacuum. A small specimen of peonidin chloride was available for direct comparison and the synthetical material showed all the properties of the material of natural origin. The appearance and shape of the crystals under the microscope, the solubility relations and colour (visual comparison of absorption spectra) of the solutions in aqueous acid and alcohol, the speed of pseudo-base formation, and the extent of recovery of colour on acidification, as well as the behaviour with potassium acetate and sodium carbonate, were all observed with identical results in the case of the two specimens. The synthetical specimen gave a weaker reaction than the natural specimen with ferric chloride, no doubt because the latter contained a trace of cyanidin.

The authors wish to thank the Royal Society for a grant which has defrayed a part of the expense of the investigation.

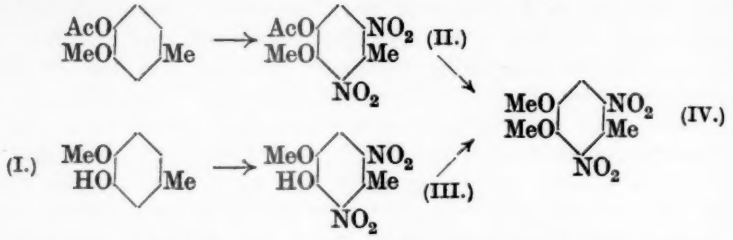
THE UNIVERSITY, MANCHESTER. [*Received, May 11th*, 1926.]

CCLXII.—*Derivatives of Homocatechol. Part I.*

By FRANZ ROBERT GRAESSER-THOMAS, JOHN MASSON GULLAND, and ROBERT ROBINSON.

A RECENT publication of Oberlin (*Arch. Pharm.*, 1925, **263**, 641) includes a description of the preparation of 2 : 6-dinitrohomoveratrole (IV) from creosol by successive acetylation, nitration, hydrolysis and methylation. We therefore submit an account of experiments in this field in which we have been engaged during the past 10 years with the ultimate object of synthesising *apo*morphine.

The annexed scheme indicates the methods which have been employed.



Pollecoff and Robinson (J., 1918, **113**, 645) showed that 2-methoxyphenyl carbonate is nitrated in the *o*- and *p*- positions with respect to the methoxyl groups alone, and this observation suggested the extension to the preparation of 2 : 6-dinitrocreosol. *iso*Creosol (I) was first obtained in poor yield by Limpach (*Ber.*, 1889, **22**, 350) by the decomposition of diazotised *m*-cresidine and was described as a yellow oil, b. p. 185°. De Vries (*Rec. trav. chim.*, 1909, **28**, 276) showed, however, that the substance has b. p. 220—222° and m. p. 35·5°, and we now submit details of a satisfactory method of preparation and confirm the properties quoted by de Vries. The phenol yields its dinitro-derivative when submitted to the action of nitrous acid or its decomposition products in ethereal solution.

Experimental.

iso*Creosol* (I).—The *m*-cresidine employed in this preparation must be of good quality, since impurities cause a decrease in the yield quite disproportionate to their amount.

Sodium nitrite (25 g.) dissolved in water (150 c.c.) was gradually added to a mechanically stirred solution of 3-amino-4-methoxytoluene (50 g.) in water (400 c.c.) and sulphuric acid (57 c.c.; *d* 1·84), maintained below 10°. The diazo-solution * was diluted with half its volume of water and dropped gradually on hydrated copper sulphate (100 g.) contained in a 1½-litre round-bottomed flask fitted with a condenser, a steam jet passing to the bottom of the vessel, and a thermometer with the bulb touching the copper sulphate. The flask was heated at 170° and a fine jet of steam was blown through the liquid in the flask during the reaction. This had the effect, not only of removing the *iso*creosol formed from the mixture, but also of breaking up the tarry scum on the surface

* In later experiments the diazo-solution was neutralised at a low temperature by the addition of copper carbonate; more regular yields (about 5%) were thus obtained.

and thus allowing the diazo-solution to come into immediate contact with the copper sulphate. The internal temperature remained almost constant at 103°. A light brown oil passed over with the steam, and the rate of addition was regulated so as to be equal to that of distillation. The addition occupied 2 hours and the steam was passed for ½ hour longer. The oil was isolated by means of ether and distilled. The fraction b. p. 200—220° (about 30 g.) was sufficiently pure for most purposes and on distillation gave 24 g., b. p. 217—218°. The colourless oil rapidly crystallised in large plates, m. p. 35—36° (Found: C, 69·5; H, 7·3. Calc. for $C_8H_{10}O_2$: C, 69·5; H, 7·2%).

*iso*Creosol gives with alcoholic ferric chloride a transitory green coloration, quickly becoming bluish-green.

Acetyl derivative. The phenol was acetylated by a boiling mixture of twice its weight of acetic anhydride and its own weight of sodium acetate for 3 hours (yield almost theoretical). The substance crystallised from a mixture of acetic acid (5 vols.) and water (3 vols.) in colourless needles, m. p. 56—57° (Found: C, 66·4; H, 6·7. $C_{10}H_{12}O_3$ requires C, 66·7; H, 6·7%). The crystals which separate from aqueous alcohol and from light petroleum are flat prisms and long needles respectively.

The *benzoyl* derivative, obtained by the usual method, crystallised from alcohol in colourless, hexagonal plates, m. p. 80—81° (Found: C, 73·8; H, 5·8. $C_{15}H_{14}O_3$ requires C, 74·4; H, 5·8%).

2 : 6-*Dinitro*-iso*creosol* (III).—A mixture of concentrated hydrochloric acid (170 c.c.) and water (200 c.c.) was gradually added with shaking to a solution of sodium nitrite (100 g.) in water (400 c.c.) underlying one of *iso*creosol (10 g.) in ether (300 c.c.). The ethereal layer became deep red and brown fumes were copiously evolved. On the following day, the ethereal solution was separated, washed with water and aqueous sodium acetate, and stirred in a concentrated solution of sodium carbonate. The precipitated yellow sodium salt was collected, washed with ether, and dried (10 g.). Its solution in water was acidified and the *dinitroisocreosol* precipitated was employed in further experiments.

The substance crystallises from water in pale yellow needles, m. p. 152—153° (decomp.) or from benzene–light petroleum in flat, yellow needles of the same m. p. (Found in material dried at 100°: N, 12·3. $C_8H_8O_6N_2$ requires N, 12·3%). The compound gives a reddish-brown coloration with alcoholic ferric chloride and its solution in sulphuric acid is orange. The yellow *sodium* salt crystallises from alcohol in felted needles and gives red solutions.

When the reaction described above was interrupted after 6 hours,

a mixture of nitrophenols could be isolated, but separation was not effected. After methylation, however, pure 6-nitrohomoveratrole, m. p. 117°, was obtained and identified.

The dinitro*iso*creosol was readily soluble in cold acetic anhydride, but was not acetylated. Reaction occurred on boiling the solution, and the resulting *acetyl* derivative crystallised from alcohol in colourless needles, m. p. 106° (Found : C, 44·9; H, 3·8; N, 10·3. $C_{10}H_{10}O_7N_2$ requires C, 44·4; H, 3·7; N, 10·4%). It gave the original compound on hydrolysis with 2*N*-sodium hydroxide on the steam-bath. It is therefore improbable that either of the nitro-groups is in the *o*- or *p*- position with respect to the methoxyl. On reduction and condensation with phenanthraquinone no phenanthraphenazine derivative was produced.

The *phenylhydrazine* salt was prepared in toluene solution and crystallised from alcohol in flat, orange needles, m. p. 109° with evolution of gas (Found : C, 45·5; H, 5·4; N, 15·8. $C_8H_8O_6N_2,C_6H_8N_2,2H_2O$ requires C, 45·2; H, 5·4; N, 15·1%). It was partially hydrolysed by boiling water and was resolved into its constituents by acids or alkalis. The *hydroxylamine* salt crystallised from water in bright orange needles which became pasty at 166° and melted to a brown liquid at 208°, a sequence not affected by recrystallisation from water or ethyl acetate (Found : C, 36·2; H, 4·4. $C_8H_8O_6N_2,NH_3O$ requires C, 36·8; H, 4·2%). On heating at 100°, the salt lost hydroxylamine, and the residue, m. p. 151°, consisted of pure dinitro*iso*creosol.

2 : 6-*Dinitroacetylcreosol* [2 : 6-*Dinitro*-4-*acetoxy*-m-*tolyl methyl ether*] (II).—Beechwood creosote was distilled through an efficient column and the fraction, b. p. 210—223°, was redistilled, the portion, b. p. 219—222°, being collected. The sodium salt was then isolated and the phenol recovered and distilled; the material, b. p. 219—221°, consisted of creosol which was sufficiently pure to be employed for most purposes.

6-*Nitroacetylcreosol* [6-*nitro*-4-*acetoxy*-m-*tolyl methyl ether*] (Cardwell and Robinson, J., 1915, **107**, 256) is best prepared by one of the following methods. (A) Acetylcreosol (25 g.) was gradually added to nitric acid (200 c.c.; *d* 1·42) cooled to — 10° and mechanically stirred. The product was precipitated by the addition of water (500 c.c.) and isolated. The nitric acid employed was previously boiled, but a trace of sodium nitrite was added just before the experiment was commenced. (B) A solution of nitric acid (10 g.; *d* 1·42) in acetic anhydride (5 c.c.) to which a crystal of urea had been added was gradually introduced into a mixture of acetylcreosol (10 g.) and acetic anhydride (10 c.c.) cooled to —10°. Water was added 15 minutes later, and the product collected. This

material (which can be used for the next stage) crystallised from alcohol in colourless, silky needles, m. p. 136—137°.

When, however, the crude product was extracted from a benzene solution with aqueous sodium hydroxide, a by-product could be isolated. The red alkaline solution was acidified with hydrochloric acid and extracted with chloroform. On evaporation of the dried extract there remained 2 g. of a yellow, crystalline mass, which crystallised from water, in which it was moderately readily soluble, in stout, yellow, hexagonal prisms, m. p. 172° (decomp.) (Found: N, 13·1. $C_7H_6O_6N_2$ requires N, 13·1%). This indicated a *dinitrohomocatechol*, and the deep cherry-red colour of its solution in aqueous alkalis as well as the rich bluish-green coloration which it gave with ferric chloride confirmed this view. On methylation with a large excess of methyl iodide and boiling alcoholic sodium ethoxide, 2 : 6-dinitrohomoveratrole, m. p. 92° (see below), was obtained. This by-product is therefore 2 : 6-*dinitrohomocatechol*. It is difficult to explain the demethylation which must have occurred.

6-Nitroacetylcreosol (4 g.) was nitrated in 1 hour by means of nitric acid (30 c.c.; *d* 1·5) below 10°. The substance crystallised from alcohol in hexagonal plates, m. p. 103° (Found: N, 10·3. Calc. for $C_{10}H_{10}O_7N_2$: N, 10·4%). On hydrolysis with 2*N*-sodium hydroxide or, better, with hot aqueous alcoholic sodium carbonate, 2 : 6-*dinitrocreosol* was obtained; this crystallised from benzene in yellow, prismatic needles, m. p. 108° (Found: C, 42·4; H, 3·6; N, 12·3. $C_8H_8O_6N_2$ requires C, 42·1; H, 3·5; N, 12·3%). When this phenol was treated with cold nitric acid (*d* 1·42), and the solution diluted with water, no precipitation occurred, but addition of a solution of quinoline in dilute sulphuric acid precipitated characteristic, bright red prisms of a *quinoline* salt; this crystallised from acetic acid in chocolate-brown, rectangular, prismatic needles, m. p. 110° (decomp.). The *quinoline* salt of 3 : 5 : 6-trinitroguaiacol (Pollecoff and Robinson, *loc. cit.*) was prepared for comparison and this crystallised from alcohol in slender, yellow needles, m. p. 185° (decomp.) (Found: N, 14·4. $C_{16}H_{12}O_8N_4$ requires N, 14·4%).

2 : 6-*Dinitrohomoveratrole* (IV) was obtained by methylation of dinitro*iso*creosol and of dinitrocreosol. In the latter case (compare Oberlin, *loc. cit.*) the aqueous alkali–methyl sulphate and the xylene–methyl sulphate–potassium carbonate method both give excellent results. A mixture of the sodium salt of dinitro*iso*creosol, anhydrous potassium carbonate (½ mol.), and methyl sulphate (about 2·5 mols.) was heated at 125° for 2 hours (yield almost quantitative). 2 : 6-Dinitrohomoveratrole crystallises from alcohol or light

petroleum (b. p. 60—80°) in colourless needles, m. p. 92° (Found : C, 44·6; H, 4·3; N, 11·5. Calc. for $C_9H_{10}O_6N_2$: C, 44·5; H, 4·1; N, 11·5%).

Anhydrocotarnine-2 : 6-dinitrohomoveratrole,

$$CH_2O_2{:}C_6H(OMe)\text{—}CH\cdot CH_2\cdot C_6H(OMe)_2(NO_2)_2$$
$$CH_2\text{—}CH_2\text{—}NMe$$

—A mixture of 2 : 6-dinitrohomoveratrole (3 g.), cotarnine (3 g.), and methyl alcohol (20 c.c.) was boiled under reflux. Crystals appeared in about 5 minutes and the reaction was completed in 10 minutes. After cooling, the substance was collected, washed with methyl alcohol, and dried in a vacuum (yield, 4·5 g.). The base crystallised from ethyl alcohol in orange-yellow, diamond-shaped plates, often arranged in stellar aggregates, m. p. 141° to a red liquid (Found : C, 54·4; H, 5·0. $C_{21}H_{23}O_9N_3$ requires C, 54·7; H, 5·0%). This substance is moderately readily soluble in benzene and, on boiling with glacial acetic acid, it is decomposed with formation of its generators.

We wish to thank the Chemical Society for a grant which has defrayed a part of the cost of the work.

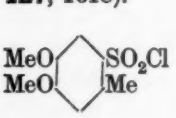
THE UNIVERSITIES OF OXFORD,
LIVERPOOL, AND MANCHESTER. [*Received, June 1st*, 1926.]

CCLXIII.—*Derivatives of Homocatechol. Part II.*

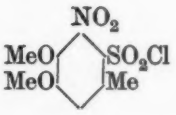
By JOHN MASSON GULLAND and ROBERT ROBINSON.

THE experiments here described were made with the object of preparing 2-nitrohomoveratrole, and the following points arising from the investigation require comment.

The nitration of homoveratrole-6-sulphonyl chloride (I) yields its 5-nitro-derivative (II) in agreement with the rule of Jones and Robinson (J., 1917, **111**, 907; compare Rây and Robinson, J., 1925, **127**, 1618).



(I.)



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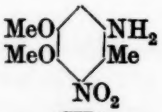

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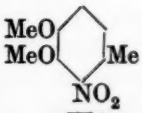


(IV.)

Oberlin (*Arch. Pharm.*, 1925, **263**, 641) reduced 2 : 6-dinitrohomoveratrole with ammonium sulphide and obtained a nitroamine, m. p. 92—93°, or 104—105°, which he considered to be homogeneous and converted into an oily nitrohomoveratrole by deamination.

Since, on oxidation, 2-nitroveratric acid was obtained, the above substances were regarded as 2-nitro-6-aminohomoveratrole (III) and 2-nitrohomoveratrole (IV), respectively.

We had traversed independently much the same ground, but our compounds were undoubtedly mixtures. Employing sodium sulphide as the reducing agent, we obtained a nitroaminohomoveratrole of m. p. 90—100°, and oxidation of the oily nitrohomoveratrole therefrom gave a mixture of nitroveratric acids.

Experimental.

5-Nitrohomoveratrole-6-sulphonyl Chloride (II).—Chlorosulphonic acid (80 c.c.) in chloroform (100 c.c.) was gradually added to a cooled, mechanically stirred solution of homoveratrole (100 g.) in chloroform (100 c.c.); as the sulphonic acid crystallised in needles, more chloroform (100 c.c.) was added. After 15 minutes, 137 g. of phosphorus pentachloride were added in four portions. The mixture was gently heated and after an hour the solution was shaken with ice-cold water, dried, and the solvent removed. The residue was triturated with light petroleum, dried (140 g.; yield 85%), and recrystallised from this solvent, homoveratrole-6-sulphonyl chloride being obtained in glistening plates, m. p. 75° (Found: S, 13·0. Calc. for $C_9H_{11}O_4ClS$: S, 12·8%). Homoveratrole-6-sulphonamide, prepared from the chloride, had m. p. 193—194° (Brown and Robinson, J., 1917, **111**, 955, describe the chloride as an oil yielding a sulphonamide, m. p. 191°).

Powdered homoveratrolesulphonyl chloride (10 g.) was gradually added to stirred nitric acid (60 c.c.; *d* 1·46), maintained below 10°, and 15 minutes later the mixture was poured into water. The product (yield, 72%) crystallised from benzene in colourless prisms, m. p. 140—141° (Found: C, 36·8; H, 3·6; N, 4·9. $C_9H_{10}O_6NClS$ requires C, 36·5; H, 3·4; N, 4·7%). To determine the position of the nitro-group, a hot solution of nitrohomoveratrolesulphonyl chloride (6 g.) in aqueous potassium hydroxide (3 g. in 80 c.c.) was cooled, the potassium salt of the sulphonic acid crystallising in elongated, rectangular plates, and concentrated sulphuric acid (70 c.c.) introduced. Superheated steam removed a yellow oil, which solidified (3·7 g.) and was then crystallised from alcohol. (i) The yellow needles (2·8 g.) were recrystallised and had m. p. 57—59° (Found: C, 54·4; H, 5·3%); after removal of a minute amount of a nitrophenol, the substance crystallised from alcohol in colourless, flat needles, which, alone or mixed with 5-nitrohomoveratrole prepared by Cousin's method (*Ann. Chim.*, 1898, **13**, 537), melted at 59° (Found: C, 54·4; H, 5·5. Calc. for $C_9H_{11}O_4N$: C, 54·8; H, 5·6%). (ii) The alcoholic mother-liquor was evaporated, the

residue extracted with cold aqueous sodium hydroxide, and the solution filtered (residue, 0·3 g. of nitrohomoveratrole). The precipitate (0·5 g.) obtained on acidification and cooling in ice crystallised from aqueous alcohol in long, orange needles, m. p. 80° (Found: N, 7·8. Calc. for $C_8H_9O_4N$: N, 7·7%). This substance yielded the above-described nitrohomoveratrole, m. p. 59°, on methylation and was unaltered in m. p. when mixed with 5-nitrocreosol (compare Oberlin, *loc. cit.*), m. p. 79—80° (Found: N, 7·6%), prepared by the nitration of creosol in ethereal solution.

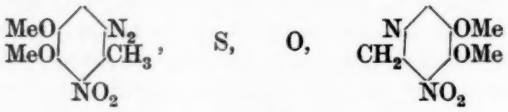
*Nitration of Acetyl*iso*creosol* [3-*Acetoxy*-p-*tolyl methyl ether*].—A series of experiments was made on the nitration of *iso*creosol in ethereal solution under various conditions and small quantities of a compound which was volatile in steam were isolated. The substance crystallised from water in needles, m. p. 166—167°, and gave a red solution in aqueous alkali, but the amount obtained did not allow of complete investigation. Under some conditions 2 : 6-dinitro*iso*creosol was obtained.

Acetyl*iso*creosol (7 g.) was gradually added to mechanically stirred and ice-cooled nitric acid (100 c.c.; *d* 1·42), the temperature being maintained below 5°. After 15 minutes, the product was precipitated by ice-water as an oil which solidified over-night (6 g.). Fractional crystallisation from alcohol gave two products. (A) The more sparingly soluble substance (yield 5 g.) crystallised from 80% alcohol in flat, yellow needles, m. p. 104—105° (Found: C, 51·0; H, 4·2; N, 6·6. $C_9H_9O_5N$ requires C, 51·2; H, 4·3; N, 6·6%). The compound gave a reddish-brown colour with ferric chloride and dissolved in aqueous alkalis to permanganate-coloured solutions. These properties and the analytical figures suggest that the substance is a nitroacetylhomocatechol the production of which would involve demethylation. After treatment for 15 minutes with boiling 2*N*-alcoholic potassium hydroxide a nitrophenol was obtained which crystallised from water in golden-yellow leaflets, m. p. 80° (unsharp), and then from light petroleum in golden-yellow needles; these melted at 82—83°, and at the same temperature when mixed with an authentic specimen of 5-nitrohomocatechol (Cousin, *loc. cit.*). In all probability, therefore, the substance, m. p. 104—105°, is 5-nitro-3-acetoxy-*p*-cresol. (B) The more soluble constituent (yield 1 g.), which was to some extent obtained from the solution by the addition of water, crystallised from light petroleum in lemon-yellow prisms, m. p. 60—61° (Found: N, 6·2. $C_{10}H_{11}O_5N$ requires N, 6·2%). It was insoluble in cold alkalis, but on boiling dissolved to an orange-red solution. The compound is doubtless a nitroacetyl*iso*creosol and very probably it is 5-*nitro*-3-*acetoxy*-p-*tolyl methyl ether*.

2-*Nitro*-6-*amino*isocreosol, $MeO{\cdot}C_6HMe(OH)(NH_2){\cdot}NO_2$.—Sodium sulphide (5 mols.) was added to a boiling solution of 2 : 6-dinitro-*iso*creosol (1 mol.) in the calculated quantity of 2% aqueous sodium hydroxide. After ¾ hour, the liquid was just acidified with hydrochloric acid, filtered while hot from sulphur, cooled, and treated with sodium acetate until it was no longer acid to Congo-red. The feathery needles obtained (yield, 25%) crystallised from methyl alcohol and then from benzene–light petroleum in orange-yellow prisms, m. p. 168—169° (decomp.) (Found: C, 49·3; H, 5·1. $C_8H_{10}O_4N_2$ requires C, 48·5; H, 5·0%). This compound is very prone to discoloration as the result of oxidation; its solution in aqueous alkalis is deep red, and it gives a green colour with alcoholic ferric chloride. The *acetyl* derivative, readily produced by the action of acetic anhydride, crystallised from water in colourless needles, m. p. 183° after slight softening at 180°. After drying in a vacuum the substance lost 6·0% at 110° (Found in dried material: N, 11·7. $C_{10}H_{12}O_5N_2,H_2O$ requires H_2O, 6·9%. $C_{10}H_{12}O_5N_2$ requires N, 11·7%). Its solution in aqueous sodium hydroxide is bright red and, on cooling to 0°, deposits the sodium salt in yellow needles. Clearly the acetyl group is attached to nitrogen, and the non-formation of a benzoxazole is one of the reasons for the assignment of the *p*-aminophenol structure to the semi-reduction product of dinitro*iso*creosol.

Nitroaminohomoveratroles and Various Derivatives.—A hot solution of crystallised sodium sulphide (25 g.) and sulphur (7·5 g.) in water (100 c.c.) was added to a boiling mixture of 2 : 6-dinitrohomoveratrole (10 g.), alcohol (50 c.c.), and water (400 c.c.). The whole was boiled under reflux for 1¼ hours, then cooled, and the precipitate of golden-yellow needles was collected and freed from sulphur by solution in hot dilute hydrochloric acid and reprecipitation by ammonia. The dry product (7·5 g.; 85%) crystallised from aqueous alcohol in golden-yellow needles, m. p. 90—100°, and no separation was effected by recrystallisation (Found: N, 13·4. Calc. for $C_9H_{12}O_4N_2$: N, 13·2%). There is no doubt that this substance is a mixture, the chief constituent of which is 2-nitro-6-aminohomoveratrole (III). The *hydrochloride*, m. p. about 210°, is hydrolysed by hot water, giving golden-yellow needles, m. p. 90—92°. The *acetyl* derivative, colourless needles, m. p. 173—175°, from alcohol, on hydrolysis yielded the original base, m. p. 90—100°. 6-*Bromo*-2-*nitrohomoveratrole*, obtained in good yield by the Sandmeyer reaction (along with a sparingly soluble *by-product*, orange needles, m. p. 241°, from ethyl acetate), crystallised from ethyl acetate in buff columns, m. p. 102° (Found: N, 5·3. $C_9H_{10}O_4NBr$ requires N, 5·1%). The action of sulphurous acid on the diazo-sulphate

from nitroaminohomoveratrole in presence of copper powder led to the production of two substances, one of which was neutral and crystallised from alcohol in golden-yellow needles, m. p. 142° (Found in material dried at 100° : C, 45·9; H, 4·3; N, 14·3; S, 6·6. $C_{18}H_{19}O_9N_5S$ requires C, 44·9; H, 4·0; N, 14·6; S, 6·7%). This curious compound, which constitutes the major product, is stable in boiling 2*N*-sodium hydroxide and dissolves in sulphuric acid to a purple solution which quickly becomes red. Apparently the following fragments



must be pieced together by suitable rearrangements in order to construct a possible constitutional formula for the substance, and this can be done in many ways. The second product from the reaction was a small amount of nitrohomoveratrolesulphinic acid. This was oxidised by permanganate, and the resulting sulphonic acid hydrolysed with superheated steam in presence of sulphuric acid. An alkali-insoluble oil and a nitrophenol, crystallising from light petroleum in needles, m. p. 62° (Found : N, 7·6. $C_8H_9O_4N$ requires N, 7·6%), were obtained. Since this nitrophenol is volatile in steam, gives a red solution in aqueous sodium hydroxide, and a green coloration with ferric chloride, it is probably 2-*nitro*-3-*hydroxy*-p-*tolyl methyl ether*. The nitrohomoveratrolediazonium chloride was reduced by stannous chloride; the resulting *nitrohydrazino-homoveratrole* crystallised from methyl alcohol in orange leaflets, m. p. 146—166°. The *piperonylidene* derivative of this hydrazine crystallised from alcohol as a mixture of small, orange-yellow tablets and large, orange-yellow plates, m. p. 171—175°. On repeated crystallisation a small amount of the plates was obtained in a homogeneous condition, m. p. 172—173°.

Nitroaminohomoveratrole itself was condensed with piperonal, and a considerable quantity of an apparently homogeneous *piperonylidene* derivative obtained which crystallised from methyl alcohol in lemon-yellow needles, m. p. 130—132° (Found : C, 59·3; H, 4·7. $C_{17}H_{16}O_6N_2$ requires C, 58·9; H, 4·7%). On hydrolysis this purified material gave a nitroaminohomoveratrole, m. p. 90—92° (Found : C, 51·2; H, 5·7. Calc. for $C_9H_{12}O_4N_2$: C, 50·9; H, 5·7%). The hydrazine prepared from this specimen crystallised from alcohol in orange leaflets, m. p. 147—149°, and in a second physical modification, m. p. 163—164° after softening at 148° (Found : N, 18·4. $C_9H_{13}O_4N_3$ requires N, 18·5%). On oxidation with copper sulphate

in dilute acetic acid solution, the last-mentioned specimen of the hydrazine gave an almost colourless oil, volatile in steam. This afforded, on oxidation with potassium permanganate, a substance, crystallising from water in needles and plates, m. p. 180—198°, which proved to be a mixture of 2-nitro- and 6-nitro-veratric acids.

We desire to thank the Chemical Society for a grant which defrayed a part of the expense of the investigation.

THE UNIVERSITIES OF OXFORD AND MANCHESTER.

[*Received, June 1st*, 1926.]

CCLXIV.—2 : 3 : 4-*Trinitrotoluene.*

By FRANK HOWORTH GORNALL and ROBERT ROBINSON.

THE purification of crude trinitrotoluene is sometimes effected by washing with cold alcohol, and on evaporation of the solvent the "trinitrotoluene residues," constituting about 10% of the original material, are obtained. The present authors have found that if the brown, pasty mass is melted and then allowed to crystallise at 18—20° after inoculation, a mixture of 2 : 4-dinitrotoluene and β-trinitrotoluene separates first and that only after 6 or 7 days is the product contaminated with the α- or the γ-isomeride. By crystallisation from sulphuric acid, the solid product yields β-trinitrotoluene in a satisfactory state of purity. A considerable number of derivatives of the substance have been obtained, but the work was carried out in special circumstances in 1917 and 1918 and we have been anticipated in several directions.

EXPERIMENTAL.

Preparation of β-*Trinitrotoluene.*—The residues (23,810 g., 21,718 g.) were melted and treated with about 10 g. of the mixture of 2 : 4-dinitrotoluene and β-trinitrotoluene obtained from a previous experiment. After a suitable interval (7 days, 5 days) the solid (6810 g., 7323 g.) was separated in a centrifuge and heated at 80—100° with concentrated sulphuric acid (3 parts). The crystals which separated on cooling, after being washed with sulphuric acid and with water and dried, melted at 108° (yield 12·3%, 13·5% of the original residue). On recrystallisation the highest m. p. observed was 112°.

If the mixture is stirred, the period required is much shortened. Residues (500 g.) stirred at 18° for 7·5 hours gave 87 g. of a solid which yielded 58 g. (11·6 %of the original residues) of β-trinitro-

toluene. We are informed that stirring is impracticable in large-scale work and the yield which can be regularly obtained is 6—7%.

A complete examination of the residues was made by taking advantage of the fact that in regard to solubility in sulphuric acid γ-trinitrotoluene is intermediate between the very sparingly soluble β-isomeride and the readily soluble dinitrotoluenes. The quantities actually isolated from 100 g. were : 2 : 4-dinitrotoluene, 47·7 g.; β-trinitrotoluene, 12·3 g.; γ-trinitrotoluene, 16·9 g. The 23 g. unaccounted for were shown to contain dinitrotoluenes and α-, β-, and γ-trinitrotoluenes. The content of β-trinitrotoluene in the residues cannot be less than 15%, nor that of γ-trinitrotoluene less than 20%.

Sodium m-*Tolylenediamine*-3-*sulphonate*, $C_6H_2Me(NH_2)_2 \cdot SO_3Na$. —The solution obtained by agitating 2 : 3 : 4-trinitrotoluene (50 g.), crystallised sodium sulphite (63·5 g.), and water (100 c.c.) at 75° was cooled; sodium 2 : 4-dinitrotoluene-3-sulphonate (55 g.) separated, and a further quantity (10 g.) could be salted from the solution (yield 90%). The substance crystallised from dilute brine in large, light amber-coloured rhombohedra (Found : H_2O, 13·6.

$C_7H_5O_7N_2SNa,2{\cdot}5H_2O$

requires H_2O, 13·7%). The anhydrous salt has been described by Brady, Hewetson, and Klein (J., 1924, **125**, 2402). On being gently heated, a solution of the sulphonate containing sodium hydroxide developed an intense permanganate colour and crystals having a bright beetle-green iridescence were deposited.

The hydrated sulphonate (100 g.), dissolved in water containing 25 c.c. of hydrochloric acid (*d* 1·16), was gradually added to a vigorously stirred mixture of boiling water with an excess of iron powder. When a drop of the liquid produced a grey spot on filter-paper (about 1 hour), the bulk was made alkaline with sodium hydroxide, filtered hot, and concentrated under diminished pressure. The *sodium* m-*tolylenediamine*-3-*sulphonate* that separated on cooling (yield 65—70%) crystallised from a little water in lustrous plates and from 80% alcohol in pearly, hexagonal leaflets (Found : S, 14·2; Na, 10·3. $C_7H_9O_3N_2SNa$ requires S, 14·3; Na, 10·3%). The substance is very readily soluble in water and sparingly soluble in absolute alcohol. It discolours at 250° and decomposes at 264°.

As a component in the preparation of azo-dyes, this salt is of some interest. All the shades are redder than those produced by the isomeric 2 : 4-diaminotoluene-5-sulphonic acid. Sulphanilic acid ⟶ *m*-tolylenediamine-3-sulphonic acid gives an orange-red, crystalline compound which dyes wool and silk in bright reddish-orange shades from an acid bath. Benzidine ⟶ *m*-tolylenediamine-3-sulphonic acid (2 mols.) gives a brilliant red dyestuff, which is

substantive to cotton. This substance is a sensitive indicator (blue when acid), and other members of the series resemble it in this respect.

When a solution of the *m*-tolylenediamine-3-sulphonate was shaken with acetic anhydride, a *monoacetyl* derivative was obtained. The free acid crystallised well from water in white needles. A number of dyes were prepared from it by diazotisation, coupling, hydrolysis, further diazotisation and coupling. The *monobenzoyl* derivative, obtained by shaking together an aqueous solution of sodium tolylenediaminesulphonate (1 mol.) and benzoyl chloride (1 mol.), crystallised from water in colourless needles (Found in material dried at 110° : C, 55·2; H, 4·8. $C_{14}H_{14}O_4N_2S$ requires C, 54·9; H, 4·6%).

Sodium 2 : 4-*Dinitro*-3-*sulphobenzoate.*—Sodium 2 : 4-dinitrotoluene-3-sulphonate (49 g.) dissolved in water (2000 c.c.) was oxidised for 6 hours at 98° with potassium permanganate (60 g.) in presence of sodium carbonate (5 g.). The excess of permanganate having been destroyed, the solution was filtered, concentrated to 300 c.c., acidified (Congo-red), and the product salted out (39 g.). It crystallised from dilute brine in colourless needles, changing in contact with the solvent into large prisms which, air-dried, lost 7·8% at 130° (Found in material dried at 130° : S, 10·0; Na, 7·2. $C_7H_3O_9N_2SNa,1{\cdot}5H_2O$ requires H_2O, 7·9%. $C_7H_3O_9N_2SNa$ requires S, 10·2; Na, 7·3%). On being strongly heated, the substance deflagrates.

The corresponding diaminosulphobenzoic acid was employed as a component in the preparation of azo-compounds. The dye from tetrazotised benzidine was a little less sensitive to acids than the corresponding product from *m*-tolylenediamine-3-sulphonic acid.

2 : 3 : 4-*Triaminotoluene.*—2 : 4-Dinitro-*m*-toluidine (30 g.) (obtained in 90% yield from 2 : 3 : 4-trinitrotoluene by heating with alcoholic ammonia) dissolved in hot alcohol containing concentrated hydrochloric acid (5 c.c.) was gradually added to a well-stirred mixture of alcohol and iron powder. When the solution became almost colourless, the alcohol was distilled under diminished pressure and the residue was taken up in water and filtered. Ferrous hydroxide was then precipitated from the hot liquid by the addition of sodium hydroxide, sufficient water being employed to dissolve the base, and charcoal also was introduced. The filtrate was acidified with hydrochloric acid; concentrated under diminished pressure, and the hydrochloride salted out (yield 12·5 g.). It crystallised in hydrated, elongated, rhombic prisms. The free *base* crystallised from ether in colourless prisms, m. p. 106° (Found : C, 61·5; H, 8·0; N, 30·1. $C_7H_{11}N_3$ requires C, 61·3; H, 8·0; N, 30·7%). It is very readily soluble in water, alcohol, or benzene,

and its solutions give a violet coloration with ferric chloride. It is very readily oxidisable and gave good results as a photographic developer, requiring, however, the addition of sodium hydroxide.

Janovsky (*Monatsh.*, 1889, **10**, 591) obtained a triaminotoluene, which he considered to be the vicinally substituted compound, by reduction of trinitroazotoluene. The m. p. of the base was not given, but the trihydrochloride was analysed. The reactions, especially that with ferric chloride, quoted by Janovsky are not in very good agreement with those of the substance described above.

2 : 4-*Dinitro*-3-*methoxytoluene* was obtained by the action of methyl-alcoholic potassium hydroxide on 2 : 3 : 4-trinitrotoluene and also by the methylation of 2 : 4-dinitro-*m*-cresol, m. p. 100°, which was prepared from 2 : 3 : 4-trinitrotoluene in several different ways, none of which gave such good results as that described by Brady, Hewetson, and Klein (*loc. cit.*). The cresol derivative was also obtained in poor yield from 2 : 4-dinitro-*m*-toluidine, which in its turn yielded 2 : 4-dinitrotoluene on deamination. These relations establish the constitution of the dinitromethoxytoluene. The substance (see the following communication) crystallises from alcohol in leaflets, m. p. 86° (Found: C, 45·2; H, 3·8; N, 13·4. $C_8H_8O_5N_2$ requires C, 45·3; H, 3·8; N, 13·2%).

Condensation of β-*Trinitrotoluene with Amines.*—This subject has been investigated by Ryan and O'Riordan (*Proc. Roy. Irish Acad.*, 1918, **34**, 175) and by Brady, Hewetson, and Klein (*loc. cit.*). 2 : 6-Dinitro-3 : 4′-dimethyldiphenylamine, obtained from *p*-toluidine, softens at 147° and melts at 152° (Ryan and O'Riordan give m. p. 131°). 2 : 4-*Dinitro*-3-*benzylaminotoluene*, from β-trinitrotoluene and benzylamine, crystallised from ethyl acetate in yellow, rhombic tablets, m. p. 115—116° (Found: N, 14·5. $C_{14}H_{13}O_4N_3$ requires N, 14·6%). A similar compound obtained from dibenzylamine crystallised from alcohol in yellow, tetrahedral rods, m. p. 87—88°. 2 : 4-*Dinitro*-m-*tolylpiperidine* was obtained from β-trinitrotoluene and an excess of piperidine. In the case of strong secondary bases alcoholic solutions should not be employed, since there is a tendency to produce the alkyloxy-compounds. The substance separates from alcohol in yellow laminæ, m. p. 101° (Found: N, 15·9. $C_{12}H_{15}O_4N_3$ requires N, 15·8%). 2 : 4-*Dinitro*-m-*tolyl*-α-*naphthylamine* crystallises from alcohol–ethyl acetate in rosettes of needles, m. p. 169—170° (decomp.) (Found: N, 13·1. $C_{17}H_{13}O_4N_3$ requires N, 13·0%). This substance gives an intense blue solution in sulphuric acid.

THE UNIVERSITIES OF LIVERPOOL AND MANCHESTER.

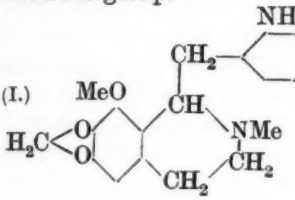
[*Received, June 1st*, 1926.]

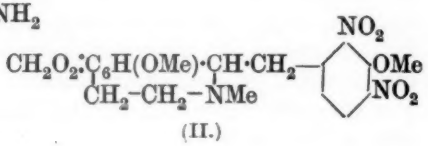
CCLXV.—*Derivatives of* 1-*Benzyltetrahydro*isoquinoline.

By ROBERT ROBINSON and HELEN WEST.

THE experiments here described were made in 1918—1919 and are now placed on record because of the extension contained in the paper which follows. As will readily be appreciated on reference to the latter memoir, it would probably facilitate the synthesis of certain alkaloids of the phenanthrene group if it were possible to prepare monoacyl derivatives of substances of the type of anhydrohydrastinine-2 : 4-diaminotoluene; whichever amino-group proved to be preferentially attacked, advantage could be taken of the process. The substance selected for examination was anhydrocotarnine-2 : 4-diaminotoluene (I), but all efforts to prepare its monoacetyl derivative were fruitless. The condensation of cotarnine and 2 : 4-dinitro-3-methoxytoluene leading to the substance (II) has also been investigated. In this case, the benzene nucleus contains substituents which by suitable modifications might be transformed into those actually occurring in the corresponding sections of the molecules of some natural alkaloids of the phenanthrene group.

(I.)





(II.)

EXPERIMENTAL.

Anhydrocotarnine-2 : 4-diaminotoluene (I).—The reduction of anhydrocotarnine-2 : 4-dinitrotoluene (Hope and Robinson, J., 1911, 99, 2114) is a troublesome operation and the yield is sensitive to variations in the conditions. The chief cause of this is the instability of the dinitro-compound in acid solution.

A mixture of crystallised stannous chloride (5 g.), granulated tin (14 g.), acetic acid (20 c.c.), and concentrated hydrochloric acid (20 c.c.) was cooled in running water and mechanically stirred. Anhydrocotarnine-2 : 4-dinitrotoluene (5 g.) was then introduced in about 4 portions in the course of ½ hour, and stirring continued for an equal period. A solution of potassium hydroxide (50 g.) in water (150 c.c.) was then added, and the precipitate was collected and dissolved as far as possible in boiling benzene. A part of the base separated from the extract on cooling; the remainder was isolated by removal of the solvent and addition of a drop of methyl

alcohol to the oily residue in order to induce crystallisation (total yield 3·8 g.). The *diamine* crystallises from methyl alcohol or benzene in colourless prisms, m. p. 119° (Found: C, 67·2; H, 6·6. $C_{19}H_{23}O_3N_3$ requires C, 66·9; H, 6·7%). When a solution in dilute hydrochloric acid is treated with sodium nitrite an orange precipitate is formed, but, nevertheless, the solution contains a tetrazonium salt and this couples with β-naphthol in alkaline solution to give a vivid vermilion azo-compound.

The *diacetyl* derivative is obtained under any conditions which suffice to acetylate the compound at all. Boiling acetic acid, cold acetic anhydride, and acetic anhydride in ethereal solution give the diacetyl derivative with more or less of the unchanged base. The derivative crystallises from alcohol in wedge-shaped needles, m. p. 211° (Found: C, 64·4; H, 6·6. $C_{23}H_{27}O_5N_3$ requires C, 64·8; H, 6·4%).

Other acylation processes were investigated, but, although benzoylation and the formation of an oxamic acid gave some promise, no well-defined monoacylation was observed in any case.

2 : 4-*Dinitro*-3-*methoxytoluene* (compare II).—A solution of sodium methoxide (4 g. of sodium) in methyl alcohol (50 c.c.) was gradually added during 5 hours to a suspension and solution of 2 : 3 : 4-trinitrotoluene (see preceding paper) (21 g.) in methyl alcohol (100 c.c.), cooled to — 4° and mechanically stirred. Stirring was continued for 7 hours at the room temperature and the mixture was then just acidified with sulphur dioxide. Most of the methyl alcohol was thereafter removed by distillation, and the residue, mixed with a little water, was heated at 70—80° in order that any unchanged trinitrotoluene might be converted into the soluble sodium dinitrotoluenesulphonate. The solid collected from the cooled mixture crystallised from aqueous alcohol (charcoal) in almost colourless, glistening plates, m. p. 86° (yield 13—16 g.). A methyl-alcoholic solution of potassium hydroxide (10 g.) in place of the sodium methoxide gives almost the same result.

A methyl-alcoholic solution of 2 : 4-dinitro-3-methoxytoluene treated with sodium hydroxide in excess develops an indigo-blue coloration, which is destroyed by water. The blue colour slowly changes to a rich magenta; the substance responsible for this effect is relatively stable to, and soluble in, water.

Anhydrocotarnine-2 : 4-*dinitro*-3-*methoxytoluene* (II).—Although many 2 : 4- and 2 : 6-dinitrotoluene derivatives condense directly with cotarnine in alcoholic solution, 2 : 4-dinitro-3-methoxytoluene gives poor results in this manner and the use of sodium methoxide as a catalyst is desirable. We found conditions which resulted in a 78% yield and the following slight modification of these, giving

a 91% yield, is due to Dr. J. Shinoda. Solutions of 2 : 4-dinitro-3-methoxytoluene (5·4 g.) in methyl alcohol (65 c.c.) and of cotarnine (6 g.) in methyl alcohol (20 c.c.) were mixed, sodium methoxide (1 g. of sodium) in methyl alcohol (5 c.c.) was introduced, and the whole kept for 50 hours. The almost pure base separated in bright yellow tablets, m. p. 135—136° (yield 10 g.). After recrystallisation from alcohol and ethyl acetate, the m. p. was 136° (Found : C, 55·4; H, 4·6. $C_{20}H_{21}O_8N_3$ requires C, 55·7; H, 4·9%). Corresponding with the fact that a catalyst is required for the satisfactory synthesis of this base is its relative stability to acids. The sparingly soluble, crystalline *hydrochloride* is colourless. On boiling with glacial acetic acid the base is slowly decomposed with formation of its generators.

Anhydrohydrastinine-2 : 4 : 6-trinitrotoluene.

$$CH_2O_2{<}\begin{matrix}C_6H_2\cdot CH\cdot CH_2\cdot C_6H_2(NO_2)_3\\ C_2H_4\cdot NMe\end{matrix}$$

—2 : 4 : 6-Trinitrotoluene (0·98 g.) was ground with methyl alcohol (20 c.c.), and hydrastinine (0·77 g.) added. The brilliant orange-yellow prisms which separated were collected, washed with methyl alcohol, and dried (yield 94%). Recrystallisation from ethyl acetate gave a product, m. p. 143° (explosive decomp.) (Found : C, 52·1; H, 3·9. $C_{18}H_{16}O_8N_4$ requires C, 51·9; H, 3·8%). This substance forms a sparingly soluble *hydrochloride* which is stable in cold dilute solution but is decomposed on boiling. The base is quickly decomposed in a hot acetic acid solution with formation of hydrastininium acetate and trinitrotoluene.

THE UNIVERSITY, LIVERPOOL. [*Received, June 1st*, 1926.]

CCLXVI.—*Synthetical Experiments in the Phenanthrene Group of the Alkaloids. Part I.*

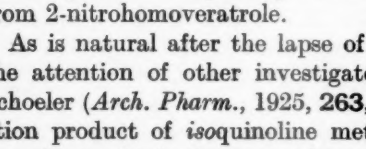
By ROBERT ROBINSON and JUNZÔ SHINODA.

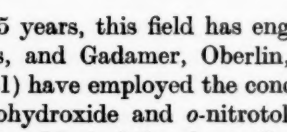
THE observations of Hope and Robinson (1911) showing that pseudo-bases of the cotarnine type can be condensed with *o*-nitrotoluene or its derivatives with formation of variously substituted 1-*o*-nitrobenzyltetrahydro*iso*quinolines cleared the way for many possible new applications of Pschorr's reaction to the synthesis of naturally occurring bases of the phenanthrene group. The condensation product from *iso*quinoline methohydroxide and 6-nitrohomoveratrole (Robinson and Robinson, J., 1914, **105**, 1456) was converted into an *iso-apo*morphine dimethyl ether, but, as already intimated (*loc. cit.*), the specimens were destroyed by fire. Not

long ago, however, a quantity of the methosulphate (I) of the final product was found in a clearly labelled tube and a description of the compound is included in this communication. The investigation is now in course of detailed repetition and it is being extended to the synthesis of *apo*morphine dimethyl ether by a similar method from 2-nitrohomoveratrole.

As is natural after the lapse of 15 years, this field has engaged the attention of other investigators, and Gadamer, Oberlin, and Schoeler (*Arch. Pharm.*, 1925, **263**, 81) have employed the condensation product of *iso*quinoline methohydroxide and *o*-nitrotoluene in order to obtain the parent base (aporphine) of the phenanthrene–*iso*quinoline group.

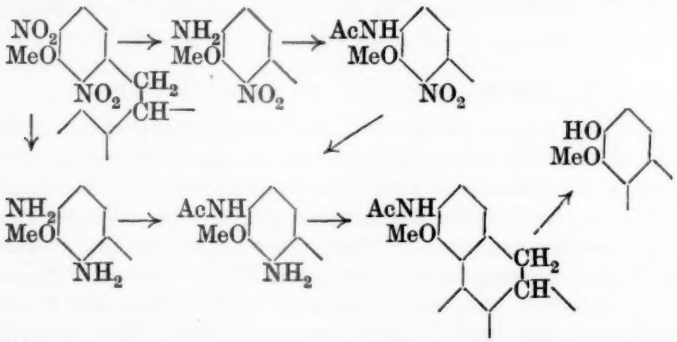
(I.)





(II.)

Assuming that 2-nitrohomoveratrole can be employed, as seems probable, for the synthesis of *apo*morphine, it does not necessarily follow that it would be equally serviceable in connexion with the bulbocapnine and corydine series, because hydrastinine has not yet been successfully condensed with a mononitrotoluene derivative. We have tried to overcome the difficulty by the use of 2 : 4-dinitro-3-methoxytoluene, which condenses very readily with pseudo-bases and is constitutionally related to 2-nitrohomoveratrole. The following scheme illustrates two of the possibilities which we had in view:

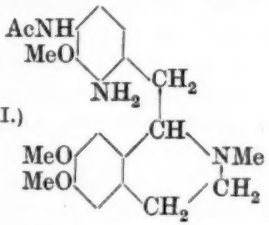


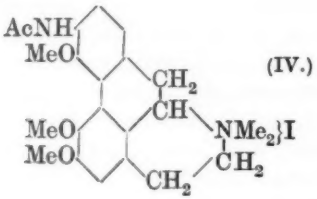
The starting-point chosen was 1-hydroxy-6 : 7-dimethoxy-2-methyl-1 : 2 : 3 : 4-tetrahydro*iso*quinoline (Pyman, J., 1909, **95**,

1266), which it is proposed * to call "laudaline" with reference to its analogy with hydrastinine and cotarnine and to the fact that it is an oxidation product of laudanosine. *Anhydrolaudaline-2 : 4-dinitro-3-methoxytoluene* (II) was obtained in good yield and reduced to a *diamine* which was analysed as the *dihydrochloride*, but mono-acetylation could not be effected and we therefore concentrated our attention on the longer process outlined above. Partial reduction with ammonium sulphide or stannous chloride gave one and the same nitroamine, and in order to determine the constitution of this we made parallel experiments with anhydrocotarnine-2 : 4-dinitro-3-methoxytoluene (II in the preceding paper). The acetyl derivative of the nitroamine from this base furnished, on oxidation with potassium permanganate in acetone solution, an acid which was identical with one prepared by the oxidation of the acetylated reduction product of 2 : 4-dinitro-3-methoxytoluene itself. Therefore the nitro-group which is reduced in the anhydrocotarnine derivative is similarly situated to that which is reduced in the dinitromethoxytoluene. Deamination of the nitroaminomethoxytoluene gave 2-nitro-*m*-tolyl methyl ether (Haworth and Lapworth, J., 1923, **123**, 2993), so that in all cases the nitro-group in position 4 is preferentially attacked. That this is true also of the anhydrolaudaline compound follows from the ultimate production of a phenanthrene derivative.

Some difficulties (see p. 1991) were encountered in the preparation of *anhydrolaudaline-2-nitro-4-acetylamino-3-methoxytoluene*, which was reduced to *anhydrolaudaline-2-amino-4-acetylamino-3-methoxytoluene* (III) by means of iron powder and acetic acid or better by hydrogen in presence of palladium.

(III.)





(IV.)

The diazonium sulphate obtained from (III), on treatment with copper powder, gave a small yield of a phenanthrene derivative, which was isolated and analysed in the form of its *methiodide* (IV). At this interesting stage our supply of the somewhat inaccessible starting material had become so small that further progress was not possible. Replacement of the acetylamino-group by hydroxyl

* After consultation with Professor Pyman.

would give a substance having one of the constitutional formulæ which may be assigned to *iso*corydine.

EXPERIMENTAL.

Anhydrolaudaline-2 : 4-*dinitro*-3-*methoxytoluene* (II).—A hot solution of "lodal" * (containing 82·4% of laudalinium chloride) (7·5 g.) and 2 : 4-dinitro-3-methoxytoluene (6 g.) in methyl alcohol (60 c.c.) was cooled and stirred during the addition of sodium methoxide (1·6 g. of sodium) dissolved in methyl alcohol (60 c.c.). The crystals which separated were collected after 48 hours and washed free from sodium chloride by water. A little unchanged dinitromethoxytoluene and a small quantity of the base could be recovered from the mother-liquor (total yield, 9·4 g.; 88·1%). The substance crystallised from methyl alcohol in large, squat, orange-yellow prisms, m. p. 111—112° (Found: C, 57·6; H, 5·6; N, 10·3. $C_{20}H_{23}O_7N_3$ requires C, 57·5; H, 5·5; N, 10·0%). The colourless *hydrochloride* crystallised from alcohol in glistening plates.

Anhydrolaudaline-2 : 4-*diamino*-3-*methoxytoluene* (II with $2NH_2$ in place of $2NO_2$).—The powdered dinitro-compound (5 g.) was added to a stirred and ice-cooled mixture of crystallised stannous chloride (5 g.), dissolved in concentrated hydrochloric acid (20 c.c.), acetic acid (20 c.c.), and granulated tin (10 g.). After 2 hours the stirring was discontinued and on the following day the solution was diluted and, after addition of an excess of potassium hydroxide, extracted with benzene. The base in the dried extract could not be induced to crystallise and therefore the *dihydrochloride* was precipitated by means of dry hydrogen chloride (yield almost quantitative). This salt crystallised from alcohol in colourless needles, m. p. 236—237° (Found: C, 55·7; H, 7·1; N, 9·4; Cl, 16·0. $C_{20}H_{27}O_3N_3,2HCl$ requires C, 55·8; H, 6·7; N, 9·7; Cl, 16·0%).

Numerous unsuccessful attempts were made to prepare the monoacetyl and monobenzoyl derivatives of the base and to condense it with oxalic acid (1 mol.). The benzoylation appeared to break the *iso*quinoline ring, since the product was devoid of basic properties.

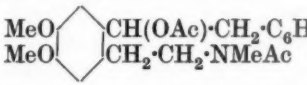
Anhydrolaudaline-2-*nitro*-4-*amino*-3-*methoxytoluene*.—(A) A hot solution of anhydrolaudaline-2 : 4-dinitro-3-methoxytoluene (5 g.) in alcohol (30 c.c.) was cooled, quickly mixed with aqueous ammonia (1·6 g.; *d* 0·880), and a current of hydrogen sulphide passed, with cooling, until 1·2 g. had been absorbed. The mixture was heated on the steam-bath under reflux for ½ hour, acidified with dilute acetic acid, filtered, and the *base* isolated by means of benzene

* The registered name of a product manufactured by Messrs. Burroughs Wellcome and Co.

after the addition of ammonia to the filtrate (yield 50%). The substance crystallised from benzene, in which it was readily soluble, in yellow plates or prisms, m. p. 145° (Found: C, 64·6; H, 6·9; N, 9·9. $C_{20}H_{25}O_5N_3,0{\cdot}5C_6H_6$ requires C, 64·7; H, 6·6; N, 9·8%). After drying at 110° in a high vacuum for 3 hours, it changed in colour, becoming yellowish-brown, and slightly decomposed (Found: C, 62·2, 62·3; H, 5·5, 5·3; N, 10·3. $C_{20}H_{25}O_5N_3$ requires C, 62·1; H, 6·4; N, 10·8%). The diazonium salt obtained from the base couples with β-naphthol, giving a crimson azo-compound.

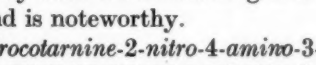
(B) The dinitro-base (5 g.), dissolved in alcohol (40 c.c.), was reduced by the addition of crystallised stannous chloride (8 g.) in alcohol (25 c.c., saturated with hydrogen chloride) during 3 hours, the mixture being stirred and cooled in ice and salt meanwhile. On the following day the base was isolated and crystallised from benzene and then from methyl alcohol; the yellow prisms obtained melted at 144°, alone or mixed with the specimen prepared by the method (A).

A solution of the nitroamine (6 g.) in acetic anhydride (20 c.c.) containing 2 or 3 drops of sulphuric acid was, after 1 hour, mixed with water; the *acetyl* derivative set free by ammonia, after being dried (4·5 g.), crystallised from dry ether in pale yellow needles, m.p. 151° (Found: C, 61·4; H, 6·2; N, 10·3. $C_{22}H_{27}O_6N_3$ requires C, 61·5; H, 6·3; N, 9·8%), which became brownish-purple on exposure to light. When anhydrolaudaline-2-nitro-4-amino-3-methoxytoluene (1 g.) was heated for 1 hour on the steam-bath with acetic anhydride (3 g.), and the product decomposed with water, a crystalline *substance* was obtained which separated from alcohol in very short, microscopic, prismatic needles, m. p. 194° (Found: C, 58·8, 58·4, 58·6; H, 6·5, 6·4, 6·1; N, 7·8. $C_{26}H_{33}O_9N_3$ requires C, 58·8; H, 6·1; N, 7·9%). The substance is devoid of basic properties and, as the indicated composition is that of the acetyl derivative (1 mol.) plus acetic anhydride (1 mol.), it is highly probable that its constitution is expressed by the formula



The facility with which the ring is broken in the production of this compound is noteworthy.

Anhydrocotarnine-2-nitro-4-amino-3-methoxytoluene,



—Anhydrocotarnine-2 : 4-dinitro-3-methoxytoluene (see preceding paper) was reduced exactly as in the case of the laudaline compound by means of alcoholic stannous chloride. The nitroamine crystallised

from benzene in minute, yellow prisms, m. p. 184° (Found: C, 60·7, 60·6, 60·6; H, 5·7, 5·6, 5·4; N, 10·5. $C_{20}H_{23}O_6N_3,0{\cdot}25C_6H_6$ requires C, 60·4; H, 5·7; N, 10·0%).* The *acetyl* derivative, obtained by the action of cold acetic anhydride in the presence of a little sulphuric acid, crystallised from ether in pale yellow prisms, m. p. 134° (Found in air-dried material: C, 57·2; H, 5·6; H_2O, 4·4. $C_{22}H_{25}O_7N_3,H_2O$ requires C, 57·2; H, 5·8; H_2O, 3·9%).

*Aceto-2-nitro-3-methoxy-*p*-toluidide*, $CH_3{\cdot}C_6H_2(OMe)(NO_2){\cdot}NHAc$. —The semi-reduction of 2 : 4-dinitro-3-methoxytoluene by ammonium sulphide or alcoholic stannous chloride gave only one nitroamine. (2 : 4-Dinitrostilbene gives 2-nitro-4-aminostilbene or 4-nitro-2-aminostilbene according as the reducing agent is ammonium sulphide or stannous chloride; Thiele and Escales, *Ber.*, 1901, **34**, 2846.)

Hydrogen sulphide was led into a cooled solution of dinitromethoxytoluene (15 g.) in alcohol (45 c.c.) to which aqueous ammonia (10 g.; *d* 0·880) had been added. When the gain in weight was 8 g., the whole was boiled under reflux for 1 hour, the alcohol distilled off, acetic acid added to the residue, and the base extracted from the filtered solution with benzene. The *hydrochloride* precipitated by passing hydrogen chloride into the dried extract was recrystallised from alcohol and then had m. p. 205° (yield 15 g.). The oily base obtained from this was at once treated with acetic anhydride and a trace of sulphuric acid; the *acetyl* derivative crystallised from methyl alcohol and from water in almost colourless, flat needles or pale yellow prisms, m. p. 108—109° (Found: C, 53·9; H, 5·3. $C_{10}H_{12}O_4N_2$ requires C, 53·6; H, 5·3%). The acetyl derivative of the product of reduction with alcoholic stannous chloride melted at 108—109°, alone or mixed with the preceding compound.

2-Nitro-4-acetylamino-3-methoxybenzoic Acid, $NHAc{\cdot}C_6H_2(OMe)(NO_2){\cdot}CO_2H$.—

(A) Potassium permanganate (8 g.) was gradually added to a well-agitated suspension of aceto-2-nitro-3-methoxy-*p*-toluidide (4·8 g.) in a solution of magnesium sulphate (8·4 g.) in water (450 c.c.) at 75—80°. Heating was continued for a short time, and the excess of permanganate was then destroyed by the addition of acetic acid and a few drops of aqueous hydrogen peroxide. The filtered solution was evaporated to a small bulk and acidified with sulphuric acid, and the crystalline precipitate thus produced was removed and dissolved in aqueous sodium carbonate and, the impurities having been extracted by ether, reprecipitated; after crystallisation from methyl alcohol and finally from water, the

* Liebermann and Lindenbaum (*Ber.*, 1902, **35**, 2917) found that acetylcochenillic acid crystallised with $\frac{1}{2}C_6H_6$.

acid was obtained in colourless needles, m. p. 228—229° (Found : C, 47·3; H, 4·1. $C_{10}H_{10}O_6N_2$ requires C, 47·2; H, 3·9%).

(B) Anhydrocotarnine-2-nitro-4-acetylamino-3-methoxytoluene was oxidised (*a*) in cold dilute acetone solution by potassium permanganate in about 24 hours, and (*b*) under conditions closely resembling those used in the case of the acetonitromethoxytoluidide. The acids isolated had m. p. 225° and 225—226°, respectively, which were not depressed on admixture with the acid, just described, of m. p. 228—229°. The properties of all the specimens were identical.

Deamination of 2-*Nitro*-3-*methoxy*-p-*toluidine*.—The crystallised hydrochloride (5 g.) of the base, prepared as described above, was dissolved in alcohol (150 c.c.), and a concentrated aqueous solution of sodium nitrite (1·8 g.) added. After 3 hours, pink crystals had separated, and the mixture was heated, at first slowly to 40—50° and after 2 hours for ½ hour on the steam-bath. A yellow oil isolated by steam distillation solidified on cooling in a freezing mixture and then crystallised from light petroleum in almost colourless prisms; these melted at 50°, alone or mixed with a specimen of 2-nitro-*m*-tolyl methyl ether, m. p. 49°, for which we are indebted to Prof. A. Lapworth and Dr. R. D. Haworth. When mixed with 4-nitro-*m*-tolyl methyl ether, m. p. 62° (Staedel and Kalb, *Annalen*, 1890, **259**, 210), the substance liquefied.

Anhydrolaudaline-2-*amino*-4-*acetylamino*-3-*methoxytoluene* (III).—(A) Iron powder (6 g.) was slowly added to a stirred solution of anhydrolaudalinenitroacetylaminomethoxytoluene (5 g.) in acetic acid (40 c.c.), which was cooled in a mixture of ice and salt. After about 6 hours, the solution was diluted, filtered, and the base extracted with benzene. The *picrate* precipitated from the dried concentrated extract by the addition of picric acid and ether crystallised from ethyl acetate in bright yellow prisms, m. p. 168—169° (Found : C, 52·4; H, 5·0; N, 12·9; H_2O, 2·6. $C_{22}H_{29}O_4N_3,C_6H_3O_7N_3,H_2O$ requires C, 52·0; H, 5·2; N, 13·0; H_2O, 2·8%).

(B) The following method is preferable to that described under (A). A solution of the nitro-base (2 g.) in acetic acid (50 c.c.) containing also an acetic acid solution of palladous chloride (10 c.c. of 2%) was agitated with hydrogen for 3 hours. The filtered liquid was basified with sodium hydroxide, and then ether extracted a *base* which crystallised from ethyl acetate in colourless needles, m. p. 110° after sintering at 105° (Found : C, 63·5; H, 7·4; N, 10·3; H_2O, 4·4. $C_{22}H_{29}O_4N_3,H_2O$ requires C, 63·3; H, 7·4; N, 10·3; H_2O, 4·8%). The yield from 3 operations was 4·0 g. The base is readily soluble in most organic solvents, crystallises from water in clusters of microscopic needles, and yields the picrate, m. p. 168—169°, described above.

Dehydro-anhydrolaudaline-4-acetylamino-3-methoxytoluene Methiodide (IV).—The amino-base (8 g.) just described was dissolved in 2·5*N*-sulphuric acid (80 c.c.) and diazotised below 0° (24 c.c. of *N*-sodium nitrite). Addition of copper powder (3 g.) after a few minutes caused the evolution of nitrogen, and after 3 hours the base in the filtered solution was isolated by means of ammonia and ether. Crystallisation could not be induced and therefore the *methiodide* was prepared. This crystallised from acetone in colourless needles (0·25 g.) which sintered at 205° and had m. p. 210° (decomp.) (Found: C, 49·9; H, 6·0; I, 22·6; H_2O, 4·7. $C_{23}H_{29}O_4N_2I,1·5H_2O$ requires C, 50·0; H, 5·8; I, 23·0; H_2O, 4·9%). The substance dissolves in sulphuric acid to a violet solution which becomes pink on heating.

iso-apo*Morphine Dimethyl Ether Methosulphate* (I).—1-(6-Nitrohomoveratryl)-2-methyl-1 : 2-dihydro*iso*quinoline (Robinson and Robinson, *loc. cit.*, p. 1459), when reduced by stannous chloride in acetic acid solution, furnished the corresponding amino-compound, which crystallised from ether. This base or the original substance, when heated with tin and concentrated hydrochloric acid in an atmosphere of hydrogen, yielded 1-(6-aminohomoveratryl)-2-methyl-1 : 2 : 3 : 4-tetrahydro*iso*quinoline as an oil. Ferric chloride developed in a dilute solution of this amine an intense blue coloration. A solution in dilute sulphuric acid was diazotised and treated with copper powder; the crude *iso-apo*morphine dimethyl ether isolated from the solution was purified through the picrate and so obtained in a crystalline condition. The crude base combined rapidly with pure methyl sulphate; the crystalline product, after several recrystallisations from water, was obtained in short, microscopic needles containing solvent of crystallisation. These dissolved when treated with alcohol, but at once separated again. The compound was crystallised from alcohol and dried at 100° (Found: C, 59·7; H, 6·5; S, 7·6. $C_{21}H_{27}O_6NS$ requires C, 59·9; H, 6·2; S, 7·6%). This salt, m. p. 246°, gives a rich royal-blue coloration with Fröhde's reagent.

6 : 7-*Dimethoxy*-1-(β-*dimethylaminoethyl*)*phenanthrene*, $C_{14}H_7(OMe)_2{\cdot}CH_2{\cdot}CH_2{\cdot}NMe_2$.—Addition of sodium hydroxide to an aqueous solution of the preceding methosulphate produced no precipitate, but an oil separated on boiling. The substance was crystallised from methyl alcohol and recrystallised from aqueous methyl alcohol and then from light petroleum, being thus obtained in large, glistening leaflets, m. p. 111° (Found: C, 77·4; H, 7·7; N, 4·5. $C_{20}H_{23}O_3N$ requires C, 77·7; H, 7·4; N, 4·5%). This base is readily soluble in most organic solvents, but is sparingly soluble in light petroleum. Its *hydro-*

chloride is sparingly soluble in dilute hydrochloric acid and crystallises in colourless needles. The base develops with Fröhde's reagent an intense green coloration, and dissolves in sulphuric acid with a bright pink colour which rapidly disappears; addition of a drop of Mandelin's reagent then produces an ivy-green coloration.

Almost at once, when the base and methyl iodide were mixed in alcoholic solution, the *methiodide* crystallised in colourless needles. Sodium hydroxide was added to the clear solution obtained on dilution with water and, on boiling, a milkiness appeared which soon gave place to a crystalline substance and at the same time trimethylamine was evolved. A crystalline, non-nitrogenous, neutral substance was isolated by means of ether.

THE UNIVERSITY, MANCHESTER. [*Received, June 1st*, 1926.]

CCLXVII.—*Pseudo-ternary Systems containing Sulphur. Part I. Sulphur and Quinoline, Pyridine, and* p-*Xylene.*

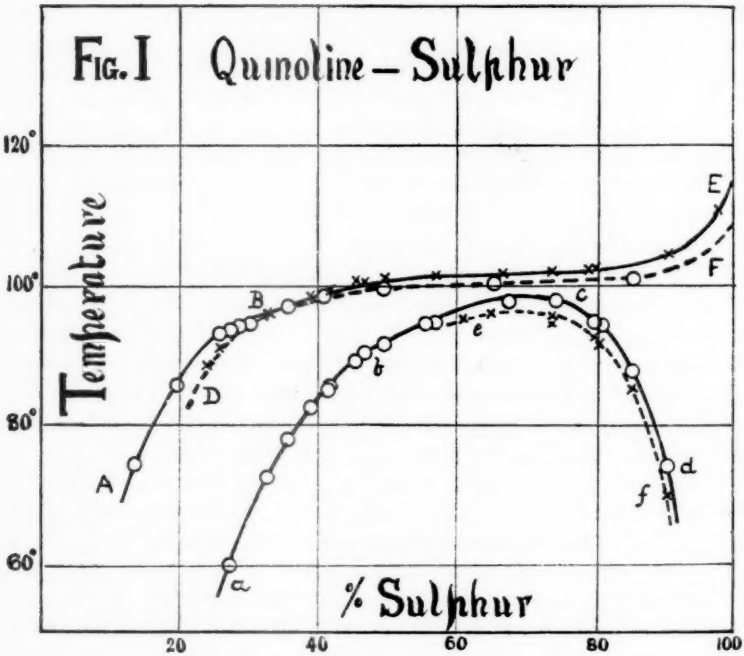
By DALZIEL LLEWELLYN HAMMICK and WILLIAM E. HOLT.

EQUILIBRIA in systems containing sulphur and an organic solvent have been studied by Smith (*J. Amer. Chem. Soc.*, 1905, **27**, 797) and by Kruyt (*Z. physikal. Chem.*, 1909, **65**, 496), who has discussed the forms of solubility curves to be expected in such systems. The experimental data, however, cover only certain ranges of concentration and temperature and, although they illustrate the possibilities predicted by Kruyt, they throw no light on the relationship between the stable, pseudo-ternary equilibria and the metastable equilibria to be obtained before equilibrium between S_λ and S_μ in the liquid phase is reached. A knowledge of this relationship is of importance in connexion with the results obtained by Äten (*Z. physikal. Chem.*, 1912, **81**, 257; 1913, **83**, 442; 1914, **86**, 1), in consequence of which he has inferred the existence of a new, very soluble form of sulphur, S_π. We have therefore investigated equilibria in the above systems by the synthetic method. As is well known, ammonia catalyses the rate of attainment of equilibrium between S_λ and S_μ and we expected that in the basic solvents pyridine and quinoline true pseudo-ternary equilibria would readily be attained. *p*-Xylene was chosen as being a non-polar solvent that could readily be obtained pure and in which the change from S_λ to S_μ might be expected to be sluggish.

The sulphur used was purified by two recrystallisations from toluene and was heated before use for several hours in a steam-

oven. Glass bulbs about 2 cm. in diameter were prepared with a neck about 10 cm. long. Weighed quantities of sulphur and solvent were introduced, the necks sealed off and drawn out to fine spindles. The tubes were then heated in a paraffin-bath, the temperature being slowly raised and the contents of the bulbs being agitated by frequent rapid rotation of the spindle. When temperatures had been reached at which the sulphur (solid or liquid) had almost disappeared, the bulbs were transferred to a thermostat, the temperature of which could be regulated to within 0·2°. By alternately

FIG. 1.



raising and lowering the temperature and noticing whether the sulphur phase increased or diminished, it was possible to fix the equilibrium temperatures to within 0·3—0·5°.

The System Sulphur–Quinoline.

Synthetic quinoline (Poulenc Frères) was distilled and found to freeze at — 18·97° (mean of three determinations). Subsequent purification by freezing out twice (half the base being crystallised each time) gave a product with m. p. — 18·93° (Bramley, J., 1916, **109**, 472, gives — 19·5° as the m. p. of pure quinoline); conse-

quently, freshly distilled quinoline was used without further purification.

In this system solid–liquid equilibria alone are stable. Points on the curve AB (Fig. 1) were obtained in the ordinary way using rhombic sulphur; the prolongation of AB to F was obtained by heating bulbs until a homogeneous phase was obtained and then either cooling rapidly to a few degrees below the temperature at which the expected solid phase should make its appearance or seeding with a trace of rhombic sulphur through a small hole in the neck of the bulb. The temperature of disappearance of the solid phase was then found in the usual way. BF thus represents metastable equilibria between rhombic sulphur and solutions. BE gives the stable equilibria between monoclinic sulphur and solutions, the metastable portion, BD, being obtained by rapid cooling as with BF. The data from which the curves ABF, DBE are plotted are in Tables I and II.

TABLE I.

Rhombic sulphur–quinoline.

% S by wt.	Temp. of equil.	% S by wt.	Temp. of equil.	% S by wt.	Temp. of equil.	% S by wt.	Temp. of equil.
13·8	74·5°	28·7	94·2°	32·95	96·0°	49·7	99·5°
19·8	85·8	30·4	94·6	41·9	98·5	65·3	100·0
25·9	93·2	32·8	96·5	49·5	99·5	85·2	101·0
*27·35	93·8						

TABLE II.

Monoclinic sulphur–quinoline.

% S by wt.	Temp. of equil.	% S by wt.	Temp. of equil.	% S by wt.	Temp. of equil.	% S by wt.	Temp. of equil.
24·0	88·75°	39·0	98·5°	49·5	101·1°	79·0	102·3°
25·9	91·0	41·9	99·2	57·0	101·4	79·8	102·5
32·8	96·0	*45·4	100·9	66·75	101·8	90·4	104·7
35·8	97·1	46·8	100·6	73·8	102·0	97·8	*111·5

The above equilibrium temperatures remained unchanged on keeping the sealed tubes; treatment of the contents of the bulbs with dry ammonia at about those temperatures also had no effect on the equilibrium temperatures. Thus the bulb corresponding to 27·35% of sulphur (marked *) in Table I was kept for 11 days, and the equilibrium temperature again found to be 93·8°. Also those marked * in Table II were kept for 17 and 13 days, respectively, and a stream of dry ammonia passed in for 20 minutes after they were opened. The bulbs were re-sealed and the temperatures of equilibrium found to be 100·9° and 111·5°.

Metastable Liquid–Liquid Equilibria.—When bulbs containing homogeneous mixtures at about 110° are cooled in the absence of solid phase, it usually happens that instead of crystalline sulphur

separating, a new liquid phase appears. The temperature at which the cloud of droplets appears is sharply defined and usually does not differ by more than 0·4° from the temperature at which it disappears sharply on warming again. On keeping the bulbs at the temperature of disappearance, crystallisation would occur after times varying from minutes in some cases to hours in others. In Table III are the data plotted as the curve *abef* in Fig. 1; the equilibrium temperatures quoted are means of observed temperatures of separation and disappearance of the cloud of second liquid phase.

TABLE III.

% S.	*T*.	% S.	*T*.	% S.	*T*.	% S.	*T*.
27·35	60·0°	45·4	89·2°	57·0	94·8°	79·0	93·9°
32·8	72·6	46·8	90·2	60·9	95·2	79·8	92·6
35·8	78·0	49·5	91·6	65·3	96·0	80·5	91·9
39·0	82·5	49·7	91·6	66·3	95·5—96·2	85·2	85·4
41·5	85·0	55·4	94·3	66·75	96·5	90·4	70·0
41·9	85·5	55·5	94·5	73·8	94·8		

Mixtures containing less than 50% of sulphur were unaffected by heating for several hours at 90° or by keeping for several weeks at room temperature. When mixtures containing more than 50% of sulphur are treated in this way, the temperature of separation slowly rises, a final temperature being reached that remains unchanged on further heating and keeping. These final values are plotted as the curve *cd* and are given in Table IV.

TABLE IV.

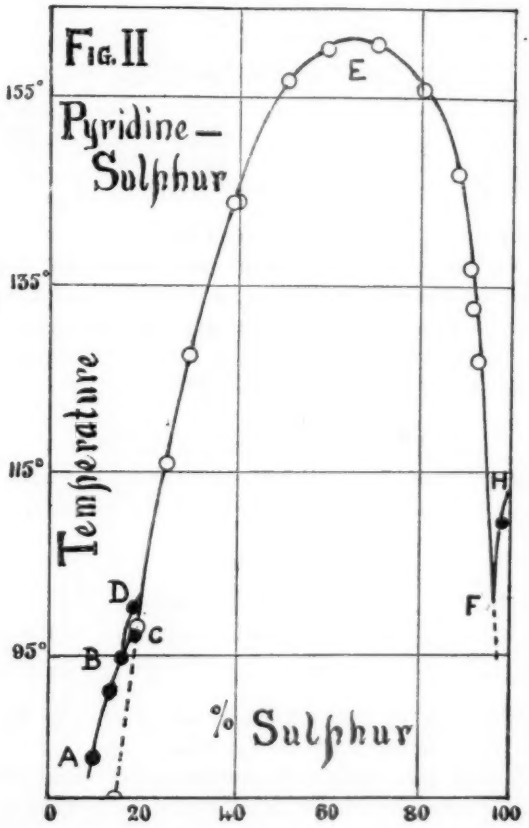
% S	49·5	49·7	66·75	73·8	79·8	80·5	85·2	90·4
T°	91·8	91·8	97·5	97·6	94·6	94·3	87·7	72·0

The curve *abcd* thus represents true (metastable) pseudo-ternary equilibria, corresponding to sulphur present as an equilibrium mixture of its various molecular species. The lower curve *ef* refers to a labile, binary system, presumably S_A–quinoline.

In order to test this view, attempts were made to estimate the amounts of S_μ present before and after internal equilibrium had been reached. Two bulbs were brought to the states represented by points on the curve *ef* and two to points on the curve *bcd*. They were then broken under a mixture of hydrochloric acid and ice, the sulphur and glass filtered off, dried and extracted with carbon disulphide. The insoluble S_μ and glass were collected and weighed together, the glass being finally weighed after the sulphur had been burned away. No weighable amount of S_μ was obtained from either of the bulbs containing labile sulphur (curve *ef*); the sulphur in the other two bulbs (curve *abcd*) contained 1·4 and 1·6% S_μ respectively.

It would thus appear that the curve *ef* represents systems in which internal equilibrium between S_λ and S_μ has not been reached. The solid–liquid systems are almost certainly pseudo-ternary, for points on the curves took several hours to determine and were unchanged after keeping the bulbs for weeks. In fact, it is rather

FIG. 2.



remarkable that with a basic solvent such as quinoline any information at all could be obtained about the labile binary system.

The System Pyridine–Sulphur.

The pyridine boiled between 114·8 and 115·3°. Equilibria were determined as in the case of quinoline, except that for temperatures above 150° a regulated air-oven was used as a thermostat. The results in Tables V and VI were obtained and are plotted in Fig. 2.

TABLE V.

Solid–Liquid Equilibria.

% S	10·05	13·35	15·9	16·9	19·2	98·0
Solution temp. (rhombic)	84·5°	91·5°	95·2°	97·5°	—	—
„ „ (monoclinic)	—	—	—	—	101·0°	110·0°

These points are shown as black dots in the figure, on the curves ABC, BD, and FH.

TABLE VI.

Liquid–Liquid Equilibria.

% S.	*T.*	% S.	*T.*	% S.	*T.*	% S.	*T.*
13·35	*ca.* 80°	38·6	144·0°	70·0	161·0°	88·4	132·5°
19·2	98·0	38·9	144·0	79·7	156·0	90·0	137·0
24·65	116·0	50·7	157·0	87·78	147·0	91·94	127·0
29·8	127·5	59·0	160·5				

These data are plotted as the curve CEF.

Several of the sulphur–pyridine mixtures were kept at the temperature of equilibrium for some hours without appreciable alteration of the equilibrium temperatures; no indication of a second liquid phase was obtained when the bulbs containing 59% and 70% of sulphur were heated to about 200°.

*The System Sulphur–*p*-Xylene.*

The *p*-xylene used was purified by freezing out and melted at 13·2°. Equilibria were determined as in the other systems.

TABLE VII.

Solid–Liquid Equilibria.

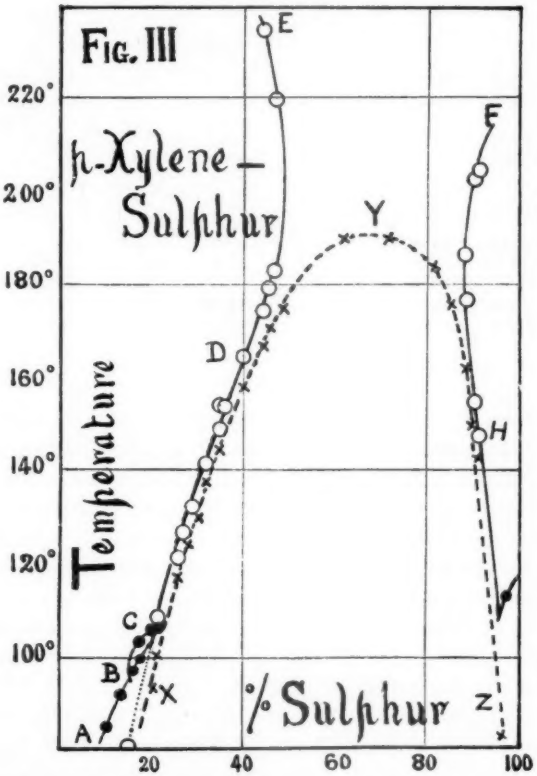
% S	21·8	16·25	13·95	16·3	20·38	17·85	11·0
Equil. temp. (rhombic)	—	—	92·5°	—	—	100·5°	85·0°
„ „ (monoclinic)	107·0°	98·2°	—	98·0°	106·0°	103·3°	—

These results are in Table VII and are plotted in Fig. 3 as the curves AB (rhombic) and BC (monoclinic).

Liquid–Liquid Equilibria.—Temperatures of complete solution found by examining freshly prepared bulbs are plotted as the curve XYZ. The paraffin-bath was stirred and heated in such a way that its temperature rose at the rate of about 2° per minute when it was about 10° below the temperature at which complete solution was expected. When bulbs were placed in the heating bath and rapidly rotated, the heterogeneous contents cleared sharply at points on the curve XYZ; these points were fixed as the means of observations made with rising and falling temperatures which did not differ by more than 1°. On keeping a bulb for a few minutes, however, under conditions represented by a point on XYZ, the

clear solution becomes cloudy owing to the reseparation of a second liquid phase and the temperature of complete solution rises until it becomes constant, after times varying from ½-hour in the case of bulbs corresponding to higher portions of the curve XYZ to a few hours in the case of those corresponding to the lower portions. These higher steady temperatures of complete solution when plotted give the curves CDE, HF. Points on the retrograde portions of the

FIG. 3.



curves CDE, HF were obtained by raising the temperature of mixtures that had become homogeneous until a new liquid phase separated.

Below about 140° the liquid phase separates in the form of fairly large drops; above 140° the cloud is composed of much smaller droplets and disappears much more sharply on raising the temperature. This fact has its effect on the experimental error, which varies from ± 1° in the lower portions of the curves to about ± 0·5° in the middle portions of the range 140—150°.

The results obtained are in Table VIII; col. 2 gives temperatures (T_1) at which the second liquid phase first dissolves; col. 3 contains the temperatures (T_2) at which the second phase finally dissolves after keeping; col. 4 gives the temperatures (T_3) at which mixtures that have become homogeneous at lower temperatures again separate into two liquid layers.

TABLE VIII.

% S by wt.	T_1.	T_2.	T_3.	% S by wt.	T_1.	T_2.	T_3.
16·25		*ca.* 80°		44·1	167·5°	174·5°	
20·38	94·0°			45·7	171·0	179·5	
21·8	101·0	109·0		46·3	175·0	183·5	220·0
25·9	117·7	121·7				Approx. equal	
27·8		127·0				cloudiness at	
27·95	124·5	129·2		48·3	175·0	196·0 and	206·0
28·04	124·2			61·7	190·0		
29·1		132·0		71·2	190·0		
30·22	130·0	133·7		81·0	184·0		
31·95	137·3	141·5		85·6	176·0		
34·6	144·5	148·25		85·5	156·0		
34·9	149·0	150·0		87·9	162·5	177·0	187·0
36·0		154·0		90·0	150·0	155·0	203·0
39·9	158·5	165·0		91·0	143·0	147·5	205·0
44·0	167·0	174·5	235·0°	96·2		84·0	

Discussion.

It has been shown that in the systems quinoline–sulphur and *p*-xylene–sulphur the attainment of internal equilibria in the phases containing liquid sulphur results in a lowering of the mutual miscibility of those phases. This effect is shown particularly well in the *p*-xylene system, in which it has been possible to determine liquid solubilities over a wide range of temperatures before and after internal equilibrium had been reached in the sulphur.

According to Äten (*loc. cit.*), liquid sulphur in internal equilibrium contains three molecular species, S_λ, S_μ and S_π, S_μ being very insoluble and S_π more soluble than S_λ. Äten gives a table of the percentages of the three forms present in molten sulphur at temperatures from 120° to 445° (*Z. physikal. Chem.*, 1913, **86**, 1). According to this, the amount of S_π present does not vary much from about 5% over the whole temperature range; S_μ, however, is present to the extent of 0·1% at 120° and increases to 1·6% at 145°. As the inflexion point in the Smith and Carson allelotropic curve for liquid sulphur is approached, the amount of S_μ increases rapidly, being 4·1% at 160° and 13·3% at 170°. On the basis of these figures we should expect, unless the internal equilibrium is very profoundly modified by the presence of the solvent *p*-xylene, that the solubility of equilibrium sulphur would exceed that of S_λ at lower temperatures. At higher temperatures, as the percentage of S_μ

increases rapidly, equilibrium sulphur should become less soluble than S_λ. These conclusions are not borne out by the results given above for the system sulphur–*p*-xylene, in which, over the whole temperature range investigated, the solubility of the liquid equilibrium sulphur is definitely less than that of the labile S_λ.

According to the views on the mutual miscibility of liquids developed by Hildebrand (*J. Amer. Chem. Soc.*, 1916, **38**, 1452; 1919, **41**, 1957; 1921, **43**, 500; etc.), non-polar liquids are incompletely miscible only when their internal pressures differ considerably and the greater the difference the higher is the critical solution temperature for the two liquids. Although it is not possible to determine values for internal pressures with any certainty, it is highly probable that they stand for xylene, toluene, and benzene in the order named (Hildebrand, *loc. cit.*). Judging from the values for the surface tension and latent heat of sulphur, its internal pressure is very much greater than those of the aromatic hydrocarbons. We should expect, therefore, that the critical solution temperatures of sulphur in the above solvents should descend in the order xylene, toluene, benzene. From Fig. 3 it appears that the critical solution temperature in xylene is 190° for S_λ; Kruyt (*loc. cit.*) found 180° in toluene and 160° in benzene for equilibrium sulphur.

Again according to Hildebrand, if one of the liquids in a binary mixture is polar (having a high value for its dielectric constant), the effect of this polarity is to diminish the mutual solubility. This conclusion receives support from the results of our experiments on the systems sulphur–pyridine and sulphur–quinoline; these are in Table IX, which includes the result of an experiment in which a mixture of alcohol and sulphur was heated in a sealed tube to above 170° without complete solution taking place.

TABLE IX.

	Diel. const.	Crit. sol. temp.
Quinoline	9·8	97°
Pyridine	12·4	160
Ethyl alcohol	26·0	>170

The internal pressures of the above three solvents are of the same order and very much less than that of sulphur.

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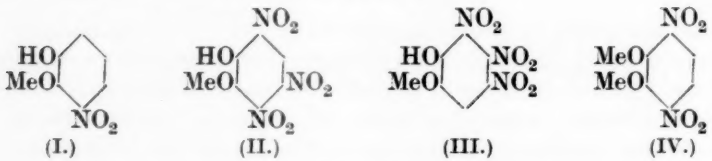
[*Received, June 1st*, 1926.]

CCLXVIII.—*New Derivatives of Guaiacol and Veratrole substituted in the* 3- *and* 6-*Positions.*

By Albert Edward Oxford.

3-Nitroguaiacol (I), hitherto the only unknown mononitro-derivative of guaiacol, has now been prepared. Benzoyl nitrate at −15° is an excellent agent for nitrating phenols and their ethers * in the ortho-position (Francis, J., 1906, **89**, 1; *Ber.*, 1906, **39**, 3798), and by means of it 3-nitro-2-methoxyphenyl acetate was obtained in minute yield from *o*-methoxyphenyl acetate, 5-nitro-2-methoxyphenyl acetate being the main product. At −40°, two-thirds of the original acetate were recovered, but the remaining third had been nitrated chiefly in the 3-position. Acetyl nitrate at −15° proved a much more satisfactory reagent, 3- and 5-nitro-2-methoxyphenyl acetates being formed in almost equal proportions, but the difficulty of effecting a complete separation of 3- from 5-nitroguaiacol somewhat diminished the final yield of the 3-isomeride. The constitution of the new nitroguaiacol follows from the fact that it yields 3-nitroveratrole on methylation and that it is not identical with 6-nitroguaiacol (Klemenc, *Monatsh.*, 1912, **33**, 701).



3-Nitroguaiacol, on further nitration in acetic acid solution, gave 3 : 4- and 3 : 6-*dinitroguaiacols* in about equal proportions, together with a small amount of 3 : 4 : 6-trinitroguaiacol (II), which can be obtained in excellent yield by the direct nitration of 3-nitroguaiacol by concentrated nitric acid, and also by the further nitration of 3 : 6-dinitroguaiacol. In the same way, 4 : 5 : 6-trinitroguaiacol (III), recently prepared (Kohn and Löff, *Monatsh.*, 1925, **45**, 605) by the partial hydrolysis of 3 : 4 : 5-trinitroveratrole, can readily be obtained by the direct nitration of 5-nitroguaiacol.

The necessary proofs of the constitution of the two new dinitroguaiacols are obtained from the observations that the one yields

* Francis's statement that veratrole is converted quantitatively into 3-nitroveratrole by this method of nitration obviously contains a clerical error, since the melting point quoted is that of 4-nitroveratrole. The present author, repeating the experiment, obtained an almost quantitative yield of 4-nitroveratrole identical in every respect with a specimen prepared from veratrole by the action of aqueous nitric acid.

3 : 4-dinitroveratrole on methylation, whilst the other yields 3 : 6-*dinitroveratrole* (IV), the diamine from which will not condense with phenanthraquinone to a derivative of phenazine. All the mono-, di,- and tri-nitro-derivatives of guaiacol and veratrole are therefore now known, with the single exception of 3 : 4 : 5-trinitroguaiacol (compare Pollecoff and Robinson, J., 1918, **113**, 647).

EXPERIMENTAL.

3-*Nitroguaiacol* (I).—Since the use of pure benzoyl nitrate, as recommended by Francis (*loc. cit.*), involves a troublesome preparation, it is much more convenient to produce the acyl nitrate *in situ*.

A mechanically stirred solution of *o*-methoxyphenyl acetate (30 g.) and redistilled acetyl chloride (25 c.c.) in pure dry carbon tetrachloride (60 c.c.), cooled in a freezing mixture and protected from moisture, is treated during 2 hours with 31 g. (a slight excess) of dry, very finely-powdered silver nitrate,* and stirring is continued one hour longer. The red liquid is then filtered from silver chloride, shaken twice with water, dried over anhydrous sodium sulphate, and, after evaporation of the solvent, distilled in a vacuum, three fractions being collected : (i) (140—170°/20 mm.), 6 g. of a yellow liquid; (ii) (170—190°/20 mm.), 18 g. of an orange liquid; (iii) (190—200°/20 mm.), 8 g. of an orange liquid.

(i) contains all the unchanged *o*-methoxyphenyl acetate, mixed with a considerable amount of 3-nitro-2-methoxyphenyl acetate; (ii) is chiefly this acetate, whilst (iii), being almost pure 5-nitro-2-methoxyphenyl acetate, solidifies on standing, and crystallises from alcohol in long, lustrous, colourless needles, melting at 101—102°, either alone or mixed with a genuine specimen prepared from *o*-methoxyphenyl acetate by Paul's method of nitration (*Ber.*, 1906, **39**, 2779).

The first two fractions are warmed on the steam-bath with 2*N*-sodium hydroxide (10 vols.), and since the success of the preparation depends upon the rapidity with which hydrolysis is carried out, the flask is corked and shaken vigorously until all the oil has dissolved (10—15 minutes). After acidification, extraction with ether and evaporation of the solvent, the crude 3-*nitroguaiacol* † is crystallised

* It is essential that the silver nitrate should be in the finest possible state of division, and this is most satisfactorily ensured by heating the finely powdered salt at 100° for several hours and repulverising immediately before use.

† Experiments with metallic nitrates other than silver nitrate gave the following results : lead and potassium nitrates were entirely inert; mercurous nitrate ($HgNO_3,2H_2O$) nitrated about 25% of the *o*-methoxyphenyl acetate, chiefly in the 3-position; cupric nitrate [$Cu(NO_3)_2,2H_2O$] gave rise to an oil, b. p. 140—150°/14 mm., which, when hydrolysed by sodium hydroxide solution free from chloride, yielded a deep red solution containing much sodium

first from light petroleum, and then thrice from carbon disulphide; it forms long, slender, very pale yellow, lustrous needles, m. p. 68·5—69·5°. The author is indebted to Mr. H. E. Buckley of the Crystallography Department of this University for the following description of these crystals (Fig. 1).

FIG. 1.

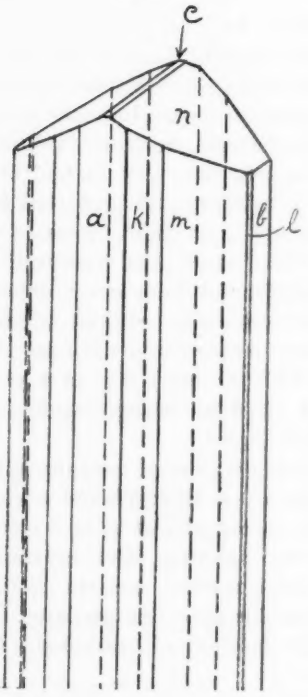
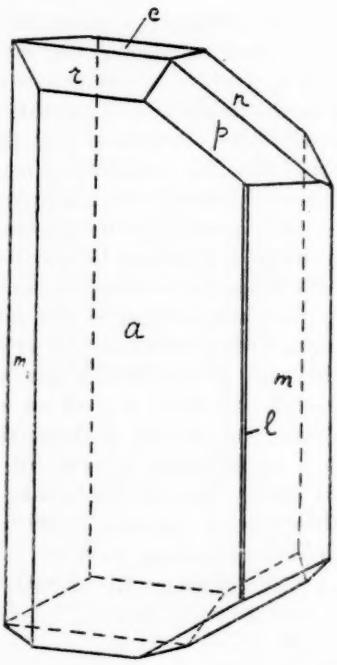


FIG. 2.



Symmetry : Rhombic, prismatic.

Axial ratios : $a : b : c = 0{\cdot}934 : 1 : 0{\cdot}584$.

Forms developed : $a = 100$, $k = 210$, $m = 110$, $l = 120$, $b = 010$, $c = 001$, $n = 011$.

Habit : Acicular, parallel to zone axis (001).

Mean angular values : *am* 43°2′, *ak* 25°7′(25°6′), *ml* 18°59′(18°47′), *bn* 59°43′, *mn* 69°25′(69°52′), *kn* 77°35½′(77°39′) (calculated values in brackets).

Cleavage : 010 perfect, 001 rare.

The crystals deposited from light petroleum (above) and from

chloride. Menke (*Rec. trav. chim.*, 1925, **44**, 146) has succeeded in simultaneously nitrating and chlorinating phenol to 4 : 6-dichloro-2-nitrophenol by the action of acetyl chloride and cupric nitrate at −14°.

carbon disulphide are identical in habit. They are readily soluble in the cold in all the usual solvents with the exception of water, carbon tetrachloride, and the two named above (Found: C, 49·6; H, 4·1; N, 8·7. $C_7H_7O_4N$ requires C, 49·7; H, 4·1; N, 8·3%).

3-Nitroguaiacol is perceptibly volatile in steam and gives a violet coloration with ferric chloride. The very soluble *sodium* salt separates as a jelly of dull red, microscopic threads when concentrated sodium hydroxide is added to a solution of the nitrophenol in saturated aqueous sodium carbonate. The *acetyl* derivative, obtained by heating the nitrophenol with acetic anhydride, is a pale yellow, uncrystallisable oil, b. p. 168—169°/12—13 mm. The *benzoyl* derivative * crystallises from alcohol in colourless, glistening plates, m. p. 88—89°. It is sparingly soluble in cold methyl alcohol. The methyl ether is identical with 3-nitroveratrole and was obtained in 96% yield from the sodium nitrophenoxide and an excess of methyl iodide in boiling methyl alcohol; after crystallisation from aqueous methyl alcohol, it had m. p. 64—65°.

3-Aminoguaiacol, obtained in small yield when 3-nitroguaiacol is reduced by hot aqueous sodium hyposulphite or by zinc and aqueous-alcoholic hydrochloric acid, crystallises from light petroleum in colourless needles, m. p. 95—96°, which rapidly become straw-brown on exposure to the air. Jona (*Centr.*, 1912, II, 1113) describes it as forming straw-coloured needles, m. p. 97—100°. It gives a brown coloration with ferric chloride.

6-*Aminoguaiacol*, obtained in excellent yield by reducing 6-nitroguaiacol † (Klemenc, *loc. cit.*) with boiling aqueous sodium hyposulphite, crystallises from light petroleum in colourless, rectangular leaflets with a silvery lustre, melting at 83·5°, and not appreciably darkening on exposure to the air (Found: C, 60·5; H, 6·9. $C_7H_9O_2N$ requires C, 60·4; H, 6·5%). It gives a port-wine colour with ferric chloride, and when boiled with excess of acetic anhydride for 4 hours appears to yield a *triacetyl* derivative, which crystallises from light petroleum in colourless, pointed needles, m. p. 122—124°

* There can be little doubt that Meldola's benzoyl-*o*-nitroguaiacol, m. p. 88—89° (P., 1896, **11**, 127; 5-nitro-2-methoxyphenyl benzoate has m. p. 102—103°), obtained in very small yield by the action of fuming nitric acid on a solution of *o*-methoxyphenyl benzoate in acetic acid, is the 3-nitro-isomeride. There is, however, no record of any subsequent investigation of this product, apart from a brief note on its reduction (J., 1898, **73**, 690). The present author found that *o*-methoxyphenyl benzoate yields a considerable proportion, but the corresponding carbonate very little, of the 3-nitro-isomeride when nitrated by acetyl chloride and silver nitrate.

† No trace of 6-nitroguaiacol could be isolated from the product from the nitration of guaiacol by acetyl chloride and silver nitrate, most of the guaiacol entirely escaping nitration at −15°. Acetyl nitrate is also without action on 6-nitro-2-methoxyphenyl acetate.

(Found : N, by micro-Dumas method, 5·5. $C_{13}H_{15}O_5N$ requires N, 5·3%).

3 : 6-*Dinitroguaiacol.*—A stirred solution of 3-nitroguaiacol (20 g.) in acetic acid (66 c.c.), cooled in ice-water, was treated with nitric acid (27 c.c.; *d* 1·42) dissolved in acetic acid (13 c.c.), the first half being added during 10 minutes and the second portion during 2 minutes. Water was added immediately, and the oil thrown down solidified on partial neutralisation of the liquid. The dry solid (7 g.) was crystallised from carbon disulphide, several times from water, and finally from light petroleum, from which it separated in yellow prisms, m. p. 69—70° (Found : C, 39·0; H, 3·1. $C_7H_6O_6N_2$ requires C, 39·2; H, 2·8%). It crystallises from water in small, thick rods, and is readily soluble in the cold in all the usual organic solvents except carbon disulphide and light petroleum. Its solution in aqueous sodium carbonate is orange-red, changing to yellow on acidification. Addition of concentrated sodium hydroxide precipitates orange-red rods of the *sodium* salt. When reduced by zinc and aqueous-alcoholic hydrochloric acid, it yields a solution of the hydrochloride of the corresponding diamine, which gives an intense permanganate colour with ferric chloride.

The *acetyl* derivative crystallises from ethyl alcohol, in which it is sparingly soluble in the cold, in very pale yellow needles, m. p. 56°. It is moderately easily soluble in cold methyl alcohol. Like 6-nitroguaiacol, 3 : 6-dinitroguaiacol could not be made to yield a benzoyl derivative by the ordinary Schotten-Baumann method and gave no coloration with ferric chloride.

3 : 6-*Dinitroveratrole* (IV), obtained in moderate yield from the above nitrophenol by the xylene–methyl sulphate–potassium carbonate method, about 30% of the nitrophenol being recovered after 3 hours' boiling, crystallises from alcohol in pale yellow, slender, flat needles, m. p. 56°, which are moderately easily soluble in cold methyl alcohol but very sparingly soluble in light petroleum (Found : C, 42·3; H, 4·0. $C_8H_8O_6N_2$ requires C, 42·1; H, 3·6%).

3 : 6-*Diaminoveratrole*, obtained by reducing the above dinitroveratrole by zinc and aqueous-alcoholic hydrochloric acid, crystallises from light petroleum in colourless needles, m. p. 82°, which turn grey almost immediately on exposure to the air (Found : C, 57·4; H, 7·3. $C_8H_{12}O_2N_2$ requires C, 57·1; H, 7·2%). It is very soluble in water, and gives an intense permanganate colour with ferric chloride. When boiled with acetic anhydride (10 parts) for 4 hours, it appears to yield a *triacetyl* derivative, which crystallises from light petroleum in clusters of colourless prisms, m. p. 96—97° (Found : N, by the micro-Dumas method, 9·5; *M*, in camphor, 308. $C_{14}H_8O_5N_2$ requires N, 9·5%; *M*, 294).

3 : 4-*Dinitroguaiacol*.—The aqueous mother-liquor from the filtration of crude 3 : 6-dinitroguaiacol was extracted with ether, yielding 9·5 g. of impure 3 : 4-isomeride. This was boiled with 120 c.c. of carbon disulphide to dissolve any 3 : 6-isomeride and then recrystallised from carbon tetrachloride several times, finally separating in colourless, microscopic plates, m. p. 109·5—110° (Found : C, 39·3; H, 2·8. $C_7H_6O_6N_2$ requires C, 39·2; H, 2·8%). It is sparingly soluble in the cold in water, carbon disulphide, carbon tetrachloride, or light petroleum, and definitely less soluble in other organic solvents than the 3 : 6-isomeride. It gives a reddish-brown colour with ferric chloride, and its *sodium* salt is precipitated in yellow, hair-like needles when sodium hydroxide is added to its solution in aqueous sodium carbonate.

The *acetyl* derivative, colourless leaflets from alcohol, melts at 99—100·5°, and the *benzoyl* derivative, colourless prisms from aqueous alcohol, at 132—133°. Both are moderately easily soluble in cold methyl alcohol, while the acetate is very sparingly soluble in cold ethyl alcohol. The *methyl* ether is identical with 3 : 4-dinitroveratrole (m. p. 91°; compare Pollecoff and Robinson, *loc. cit.*), and is readily obtained by means of the xylene–methyl sulphate–potassium carbonate method.

Both 3 : 4-dinitroguaiacol and its methyl ether, when reduced by zinc and aqueous-alcoholic hydrochloric acid, yield diamines which condense with the bisulphite compound of phenanthraquinone to give the corresponding ethers of 1 : 2-dihydroxyphenanthraphenazine; these exhibit a green fluorescence in benzene solution, and a dull magenta tint with concentrated sulphuric acid. 3 : 4-Diaminoguaiacol gives a permanganate colour with ferric chloride only slightly less intense than that given by the 3 : 6-isomeride.

3 : 4 : 6-*Trinitroguaiacol* (II).—3-Nitroguaiacol (2 g.), cooled by running water, was nitrated with 9 c.c. of nitric acid (*d* 1·42); the product crystallised after a few minutes and was collected after the addition of water (yield 1·5 g.).

This trinitroguaiacol was obtained in small quantity by extracting the mother-liquor of the dinitroguaiacols with ether, and also by the further nitration of 3 : 6-dinitroguaiacol : 0·1 g. of the latter dissolved in 0·5 c.c. of cold concentrated nitric acid slowly deposited crystals of the trinitroguaiacol.

3 : 4 : 6-Trinitroguaiacol is dimorphous : one modification, pale yellow leaflets, m. p. 108—109°, is obtained by crystallisation from water or by slow deposition from carbon tetrachloride solution, and the higher-melting form, very pale yellow, flat needles, m. p. 113·5°, by rapid crystallisation from a hot concentrated carbon tetrachloride solution or from benzene containing a little light

petroleum. Well-formed crystals (Fig. 2) can be obtained by very slow crystallisation from the last-named solvents, and the author is indebted to Mr. H. E. Buckley for the following description of them:

System: Monoclinic sphenoidal (digonal polar). Axial ratios: $a : b : c = 1{\cdot}429 : 1 : 0{\cdot}622$, $\beta = 97°35'$. Habit, somewhat tabular on $a(100)$. The following forms are usually present: $a = 100$, $m = 110$, $r = 101$, $c = 001$, $n = 011$, $p = 111$ and less frequently $l = 210$. Mean angular values: *ar* 72°59′, *rc* 24°36′, *am* 54°47′, *ap* 75°41′(75°26′), *an* 96°41′(96°27′), *np* 20°56′(21°1′), *al* 35°17′(35°19′), *cn* 32°5′(31°40′) (calculated values in brackets). Cleavage: good parallel to *c*, fair parallel to *a*.

Optical properties: there is a straight extinction parallel to edge $a : m$ and to edges $c : n$ and $c : r$ in accordance with the symmetry, but no sign of an interference figure could be obtained in any of the expected directions. This would indicate the possibility of a still lower class of symmetry, *viz.*, anorthic pedial.

The two modifications also differ as regards decomposition point. The higher-melting form always begins to evolve gas at 131°, but the decomposition point of the lower-melting form varies with the rate of heating and may lie anywhere between 145° and 175°. Below 131°, the melt always resolidifies to the higher-melting modification. In combustions a high result was always obtained for carbon, and even a micro-Dumas estimation gave a slightly low result for nitrogen (Found: N, 15·9. $C_7H_5O_8N_3$ requires N, 16·2%).

This trinitroguaiacol, which is but sparingly soluble in cold water to a pale yellow solution, dissolves in aqueous sodium carbonate with evolution of carbon dioxide and, as might be predicted from its constitution, is much more sensitive to caustic alkalis than either of its known isomerides.

Addition of concentrated sodium hydroxide to its solution in aqueous sodium carbonate precipitates a yellow *sodium* salt, which redissolves almost immediately to give a deep red solution. A solution of the trinitroguaiacol in 10% aqueous sodium hydroxide, yellow at first, becomes rose-red in 2 minutes, and a very deep shade of red in 30 minutes. The solution then contains sodium nitrite and yields no precipitate on acidification.

Its solution in ammonia or in aqueous sodium carbonate also develops a permanent red colour on boiling.

When boiled with methyl sulphate and potassium carbonate in xylene solution, 3 : 4 : 6-trinitroguaiacol entirely escapes methylation and is slowly decomposed.

The *benzoyl* derivative crystallises from aqueous alcohol in nearly colourless, short needles, m. p. 146—147°. It is moderately soluble in cold alcohol.

The *quinoline* salt is immediately precipitated when a solution of quinoline sulphate in very dilute sulphuric acid is added to a dilute aqueous solution of the trinitroguaiacol. It crystallises from chloroform–light petroleum in intensely yellow, minute prisms which soften at 185° and decompose at 190° (Found: N, by the micro-Dumas method, 14·1. $C_7H_5O_8N_3,C_9H_7N$ requires N, 14·4%). This derivative was also isolated from the original nitric acid solution from which the crude 3 : 4 : 6-trinitroguaiacol was separated, the proof of identity being the comparison of decomposition points under simultaneous heating. Hence, 3 : 4 : 6-trinitroguaiacol is the only trinitroguaiacol produced by the direct nitration of 3-nitroguaiacol.

The *pyridine* salt, yellow, ill-defined prisms from methyl alcohol, softens at 146° and melts at 150—153° (decomp.).

4 : 5 : 6-*Trinitroguaiacol* (III).—5-Nitroguaiacol (9 g.) nitrated exactly as described in the preparation of 3 : 4 : 6-trinitroguaiacol (above), except that the beaker was cooled in ice, yielded 4·5 g. of the crude trinitroguaiacol, which crystallised from chloroform–light petroleum in small, very pale yellow needles, m. p. 144—147° (decomp.) (Found: N, by the micro-Dumas method, 16·3%). The benzoyl derivative melts at 140—143°, and the quinoline salt, small, yellow, elongated, rectangular plates from chloroform–light petroleum, at 207—209° (decomp.), with darkening at 203°. Kohn and Löff (*loc. cit.*) quote m. p.'s 143—149° (decomp.), 146°, and 201° (decomp.), respectively.

This trinitroguaiacol is sparingly soluble in water to a distinctly orange solution, and dissolves momentarily in saturated aqueous sodium carbonate with evolution of carbon dioxide, after which a copious yellow precipitate of the sodium salt is thrown down.

I wish to thank Professor R. Robinson, F.R.S., for his interest in this work.

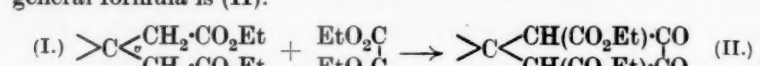
THE UNIVERSITY, MANCHESTER. [*Received, May 10th*, 1926.]

CCLXIX.—*Formation and Stability of* spiro-*Compounds. Part XIII.* spiro-*Compounds from the Substituted Lævulic Acids.*

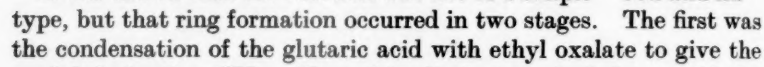
By EUGENE ROTHSTEIN and JOCELYN FIELD THORPE.

BY condensing oxalic ester with various substituted glutaric acids (the Dieckmann-Komppa reaction) Dickens, Kon, and Thorpe

(J., 1922, **121**, 1496) obtained a series of cyclic diones whose general formula is (II).



It was shown that the reaction was not of a simple " box and lid " type, but that ring formation occurred in two stages. The first was the condensation of the glutaric acid with ethyl oxalate to give the oxalyl derivative (III). Next this eliminated alcohol to yield the cyclic dione (II).



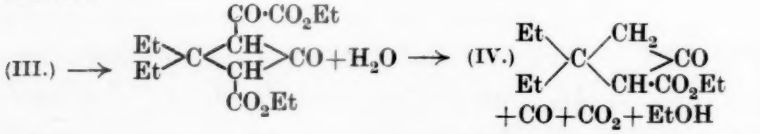
The yields obtained are in Table I.

TABLE I.

Oxalic ester with ester of	Angle θ.	Yield of *cyclo*-pentanedione.
Glutaric acid	115·3°	80%
β-Methylglutaric acid	112·5	Almost quantitative.
*cyclo*Pentanediacetic acid	109·5	60—70%
ββ-Dimethylglutaric acid	109·3	66%
ββ-Methylethylglutaric acid	?	20%
ββ-Diethylglutaric acid	?	Nil
*cyclo*Hexanediacetic acid	107·2	Nil

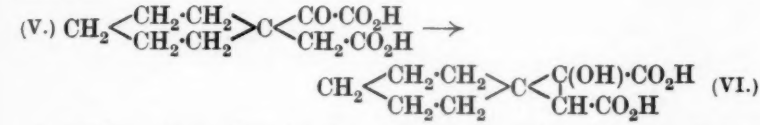
The greatest yield of dione is given by glutaric ester itself, the angle θ of which is far greater than that required to form a stable *cyclo*pentane ring. The alteration of this angle must therefore have been caused by the presence of the oxalyl group on the α-carbon atom, and the ring itself stabilised by the 2 : 5-carbethoxy-groups. The effect of further deflection of the angle θ by means of a *gem*-grouping, such as diethyl or the *cyclo*hexane ring, would be to make the formation of the *cyclo*pentane complex more difficult, and in some cases impossible.

This view was confirmed in the case of the diethyl compound by the formation of a small quantity of a four-membered cyclic compound (IV) the synthesis of which must be represented as follows :



It was of course expected that *cyclo*hexanediacetic ester also would yield a four-membered cyclic compound, but Dickens, Kon, and Thorpe were unable to isolate it, a fact which they attributed to the experimental difficulties encountered in working with *cyclo*-

hexane compounds. There was no necessity, however, for such an assumption. It was shown subsequently (Lanfear and Thorpe, J., 1923, **123**, 2865) that α-keto*cyclo*hexanediacetic acid (V) is completely converted into *cyclo*hexane*spirocyclo*propan-2-ol-2 : 3-dicarboxylic acid (VI) when boiled with strong potassium hydroxide solution.

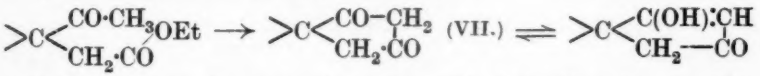


(V.) (VI.)

It follows, then, that in the *cyclo*hexane series the carbethoxy-groups of the oxalyl derivative (III) deflected the angle θ even further than was necessary for the formation of the four-membered ring, and that as the conditions for the production of the *spirocyclo*propane ring were absent, no cyclic derivative could be isolated.

To test the truth of this deduction, it was decided to substitute hydrogen atoms for the two carbethoxy-groups. Under these conditions it was to be expected that the yield of the dimethyl-*cyclo*pentane compound would be decreased, whereas the yield of the *cyclo*hexane*spirocyclo*pentane derivative should be increased. In the case of the compound (V), the formation of a *cyclo*propane ring would no longer be possible.

A series of *cyclo*pentane compounds (VII) was prepared from the corresponding lævulic esters by direct ring closure through the action of dry sodium ethoxide in a manner analogous to that used by Vorländer in his synthesis of dihydroresorcinol from δ-keto-butyric ester (*Annalen*, 1896, **294**, 270).



(VII.)

Table II shows that not only is the yield of the dione increased in the case of the *cyclo*hexane compound, but that the order of stability given in Table I is reversed.

TABLE II.

Ester used.	% Yield of *cyclo*pentanedione.
ββ-Dimethyl-lævulic	20—25
ββδ-Trimethyl-lævulic	35 *
1-Acetyl*cyclo*hexane-1-acetic	48

* De Rosanbo, *Ann. Chim.*, 1923, [ix], **19**, 327.

Attempts made by De Rosanbo (*loc. cit.*) and by the authors to obtain *cyclo*pentane-1 : 3-dione from lævulic acid itself failed owing to the tendency of the latter to form unsaturated lactonic compounds.

Trimethyl-lævulic acid gives a higher yield of the dione than the dimethyl compound (Table II). This is to be expected, since the introduction of another methyl group necessarily decreases the distance between the terminal carboxyl group and the terminal methyl group. The deflection caused by this group is not as great as in the case of the carbethoxyl or carboxyl group, as will become evident.

Ethyl 1-*acetyl*cyclo*hexane*-1-*acetate* (VIII) was prepared by the action of zinc methyl iodide on the acid chloride of ethyl 1-carboxy-*cyclo*hexane-1-acetate (IX) (compare ββ-dimethyl-lævulic acid; Rothstein, Stevenson, and Thorpe, J., 1925, **127**, 1072).

(IX.) $CH_2<\begin{matrix}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{matrix}>C<\begin{matrix}COCl\\CH_2\cdot CO_2Et\end{matrix}\longrightarrow$

$CH_2<\begin{matrix}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{matrix}>C<\begin{matrix}CO\cdot CH_3\\CH_2\cdot CO_2Et\end{matrix}$ (VIII.)

The *acid* obtained by its hydrolysis gave a theoretical yield of the *semicarbazone* and was extremely stable to reagents. It distilled without decomposition, and neither sulphuric acid (25%) nor potassium hydroxide solution (75%) had any action upon it. In the latter respect it differs markedly from α-keto*cyclo*hexanediacetic acid (V), which is completely changed to *cyclo*hexane*spirocyclo*pentan-2-ol-2 : 3-dicarboxylic acid.

This difference in behaviour is only to be expected, since it is another illustration of the great deflection of the tetrahedral angle due to the carboxyl group. The substitution of an α-methyl group for the corresponding carboxyl group in α-keto*cyclo*hexanediacetic acid increases the angle θ, and the α′ and α-carbon atoms are no longer close enough for the closure of the *cyclo*propane ring to occur. The increase of the angle θ, however, separates the α-methyl group and the α′-carbon atom, thus introducing the possibility of the formation of the five-membered ring (VII).

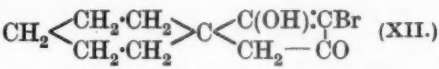
In fact, the formation of cyclo*hexane*spirocyclo*pentane*-2 : 4-*dione* (X) proceeded quite easily. The compound was a crystalline solid giving a deep crimson colour with alcoholic ferric chloride. Its

(X.) $CH_2<\begin{matrix}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{matrix}>C<\begin{matrix}CO-CH_2\\|\\CH_2\cdot CO\end{matrix}\rightleftharpoons$

$CH_2<\begin{matrix}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{matrix}>C<\begin{matrix}C(OH):CH\\|\\CH_2-CO\end{matrix}$ (XI.)

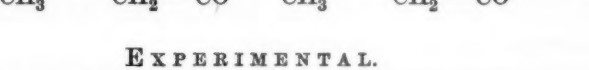
constitution was shown by oxidation with alkaline sodium hypochlorite, 1-carboxy*cyclo*hexane-1-acetic acid being produced. When

treated with the theoretical quantity of bromine, it gave a quantitative yield of the *bromide* (XII).



(XI.) (XII.)

1 : 1-Dimethyl*cyclo*pentane-2 : 4-dione (or 1 : 1-dimethyl-Δ^2-*cyclo*penten-2-ol-4-one; XIII) could not be isolated from the syrupy products formed by the action of sodium ethoxide on ethyl ββ-dimethyl-lævulate. The yield was therefore estimated by titration with bromine (compare experimental portion). A solid *bromide* (XIV) was isolated in an 18% yield.



(XIII.) (XIV.)

Experimental.

Anhydride of 1-*Carboxy*cyclo*hexane*-1-*acetic Acid*.—In the preparation of 1-carboxy*cyclo*hexane-1-acetic acid by Lapworth and McRae's method (J., 1922, **121**, 2754) it was found better to hydrolyse the dicyano-ester, C_5H_{10}:C(CN)·CH(CN)·CO_2Et, with 75% sulphuric acid instead of fuming hydrochloric acid as described. The hydrolysis product was distilled in steam to remove traces of unchanged nitrogen compounds. An acid was obtained which after recrystallisation from benzene and petroleum melted at 134° and not 132° as given in the above paper (Found: C, 58·4; H, 7·7. Calc.: C, 58·0; H, 7·5%).

The anhydride was best obtained by distilling the acid under reduced pressure through a wide air condenser. It volatilised with the steam produced and it was necessary to take precautions to prevent the pump being blocked. The anhydride separated from petroleum (b. p. 40—60°) in shimmering leaflets, m. p. 55° (yield 76%) (Found: C, 64·6; H, 7·3. Calc.: C, 64·3; H, 7·1%).

Ethyl 1-*Acetyl*cyclo*hexane*-1-*acetate* (VIII).—A solution of sodium (8·9 g.) in absolute ethyl alcohol (100 c.c.) was added slowly with shaking to the pure recrystallised anhydride (65 g.), also dissolved in absolute ethyl alcohol (50 c.c.). The alcohol was removed in a vacuum, and after acidification the heavy oil was extracted with ether. The ethereal extract yielded a thick, almost colourless syrup, which subsequent treatment showed to be almost entirely ethyl 1-carboxy*cyclo*hexane-1-acetate, b. p. 175—180°/11 mm. (yield 70 g.).

The crude acid ester (60 g.) was converted into the acid chloride with thionyl chloride (30 c.c.) in the usual way. The crude chloride,

diluted with an equal bulk of benzene, was added during 45 minutes to zinc methyl iodide, methyl acetate being used instead of ethyl acetate in the preparation of the latter compound. (Unless these precautions were taken, the yield was reduced to a negligible quantity.) The product, after standing an hour, was worked up in the usual way; b. p. 144—154°/14 mm. (yield 20—30 g.).

1-*Acetyl*cyclo*hexane*-1-*acetic Acid*.—The above ester was boiled under reflux with potassium hydroxide (50%) and an equal bulk of ethyl alcohol. The sticky solid obtained on acidification became crystalline after being rubbed with petroleum–ether.

The crude acid (9·5 g.) yielded 10 g. of a *semicarbazone*, m. p. 212° after recrystallisation from ethyl alcohol and water (Found: C, 55·0; H, 8·0; N, 17·2. $C_{11}H_{19}O_3N_3$ requires C, 54·8; H, 7·9; N, 17·4%). From the aqueous filtrate, ether extracted 4·7 g. of 1-carboxy*cyclo*hexane-1-acetic acid.

The crude mixture (which, as shown above, contained 80% of the keto-acid) was distilled; b. p. 140—200°/20 mm. The distillate was extracted with saturated sodium hydrogen carbonate solution, and the extract on acidification yielded the pure ketonic acid which, after two crystallisations from benzene and petroleum, melted at 82° (Found: C, 65·2; H, 8·8. $C_{10}H_{16}O_3$ requires C, 65·2; H, 8·7%).

The ketonic acid is remarkably stable, resisting attack by phosphorus pentabromide, phosphorus trichloride, acetyl chloride, and phenylcarbimide.

The *ethyl* ester, b. p. 155°/15 mm., was prepared from the pure acid by Phelp and Tillotson's alcohol vapour method (yield 94%). It gave neither a semicarbazone nor any derivative with acetyl chloride or phenylcarbimide.

cyclo*Hexane*spirocyclo*pentane*-2 : 4-*dione* (X).—Ethyl 1-acetyl-*cyclo*hexane-1-acetate (13 g.) was treated with dry sodium ethoxide in ethereal solution by a method similar to that used by De Rosanbo (*loc. cit.*) in the preparation of 1 : 1 : 3-trimethyl*cyclo*pentane-2 : 4-dione from ββδ-trimethyl-lævulic acid. The product was rubbed with dry ether and recrystallised from ethyl alcohol and water; m. p. 180° (yield 48%) (Found: C, 72·3; H, 8·1. $C_{10}H_{14}O_2$ requires C, 72·3; H, 8·4%). The compound decolorised cold alkaline potassium permanganate and was unchanged by boiling 50% potassium hydroxide solution.

Oxidation with sodium hypochlorite. The *spiro*-compound (1 g.) dissolved in a small quantity of potassium hydroxide solution was added cautiously to 25% sodium hypochlorite solution (15 c.c.), cooled in ice. After being shaken, the mixture was kept for 30 minutes, acidified, and extracted with ether. The extract yielded

1-carboxy*cyclo*hexane-1-acetic acid, m. p. 130—131°, from which the anhydride was prepared.

Enol content. Titration with bromine by Meyer and Kapelheir's method (*Ber.*, 1911, **44**, 2718) showed a 69·4% enolisation of both keto-groups.

cyclo*Hexane*spiro-3-*bromo*-Δ^2-cyclo*penten*-2-*ol*-4-*one* (XII).—The *spiro*-compound (2 g.), suspended in chloroform, dissolved on addition of a chloroform solution of bromine (2 g.). The solution was evaporated on the steam-bath; the solid obtained was recrystallised from ethyl alcohol and water; m. p. 238° (Found: C, 48·5; H, 5·2. $C_{10}H_{13}O_2Br$ requires C, 49·0; H, 5·3%). The compound was strongly acidic, decomposing sodium hydrogen carbonate. An alcoholic solution gave an intense crimson colour with neutral ferric chloride.

1 : 1-*Dimethyl*cyclo*pentane*-2 : 4-*dione* (1 : 1-*Dimethyl*-Δ^2-cyclo*penten*-2-*ol*-4-*one*) (XIII).—Ethyl ββ-dimethyl-lævulate was treated with sodium ethoxide in the same way as the *cyclo*hexane ester. A syrup was obtained which did not solidify. As this compound had been isolated before (Farmer, Ingold, and Thorpe, J., 1922, **121**, 128), the purification was not proceeded with, but the yield was estimated by means of bromine titrations. Although it could not be estimated exactly, it was considered that the amount of enolisation would probably be equal to that of the *cyclo*hexane*spiro*-compound. Assuming this, it was found that the yield was between 20% and 25%. This figure was confirmed by the formation of 3-*bromo*-1 : 1-*dimethyl*-Δ^2-cyclo*penten*-2-*ol*-4-*one* (XIV), which was obtained by the action of a chloroform solution of bromine (0·9 g.) on a solution of the syrup (1·3 g.) in chloroform. After evaporation, a gummy residue was obtained which partly solidified. The adhering syrup was removed by rubbing with chloroform–petroleum; the solid then crystallised from ethyl alcohol and water in clusters of prisms, m. p. 203° (yield 18%) (Found: C, 40·8; H, 4·0. $C_7H_9O_2Br$ requires C, 41·0; H, 4·3%). The bromide is insoluble in benzene, is strongly acidic, and gives a blood-red colour with alcoholic ferric chloride.

We are indebted to the Chemical Society for a grant which has partly defrayed the cost of the materials required for the investigation.

THE IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
SOUTH KENSINGTON. [*Received, June 1st*, 1926.]

CCLXX.—*Researches on Residual Affinity and Co-ordination. Part XXVII. Ethylenediammine Copper Salts.*

By GILBERT T. MORGAN and FRANCIS HEREWARD BURSTALL.

AMONG acidic radicals which favour the reversion of copper to its fundamental univalency are the cyanide, iodide, thiocyanate, and xanthate, so that cupric salts of these radicals pass spontaneously into cuprous compounds even in aqueous media at the ordinary temperature. This change of valency can, however, be hindered by certain addenda of crystallisation or co-ordination which tend to retain the metallic atom in the alternative condition of bivalency.

In accordance with the electronic conception of atomic structure and chemical combination, this change from univalent to bivalent copper corresponds with a displacement of an electron from a complete inner sub-group to the outermost group of valency electrons: Cu^{I} 2. 224. 22446. **1** to Cu^{II} 2. 224. 22445. **2** (Main Smith, *J. Soc. Chem. Ind.*, 1924, **43**, 323). The latter arrangement is less symmetrical as regards inner electrons and suggests a strained condition manifested generally by the appearance of visible colour.

The experiments described below indicate the extent to which cupric iodide and cyanide can be stabilised by means of ethylenediamine.

I. *Amminated Cupric Iodides.*

It was already known that ammonia had a stabilising effect on cupric iodide and several ammino-derivatives have been described. Monoaquotetramminocupric iodide, $[Cu,4NH_3,H_2O]I_2$, has been prepared by a variety of processes (Berthelot, *J. Pharm.*, 1830, **15**, 445; Rammelsberg, *Pogg. Ann.*, 1839, **48**, 162; Saglier, *Compt. rend.*, 1886, **102**, 1554; Pozzi Escot, *ibid.*, 1900, **130**, 90; Horn, *Amer. Chem. J.*, 1908, **39**, 204). A polynuclear compound, decamminocupric iodide, $3CuI_2,10NH_3$, has also been obtained (Richards and Oenslager, *Amer. Chem. J.*, 1895, **17**, 302; Saglier, *loc. cit.*; Kohlschütter and Pudschies, *Ber.*, 1904, **37**, 1153; Ephraim, *Ber.*, 1919, **52**, 940). A readily dissociable hexamminocupric iodide, $[Cu,6NH_3]I_2$, has been studied by Richards and Oenslager, Horn, and Ephraim (*loc. cit.*), and the last-mentioned investigator has indicated a pentammine, $CuI_2,5NH_3$, and a diammine, $CuI_2,2NH_3$.

In earlier researches on ethylenediamminocupric salts Grossman and Schück (*Z. anorg. Chem.*, 1906, **50**, 15), who prepared the chloride and bromide of the general formula CuX_2,en,H_2O, also isolated a bromide, $CuBr_2,2en,2H_2O$, corresponding with the chloride, $CuCl_2,2en,2H_2O$, already produced by Werner and Spruck

(*ibid.*, 1899, **21**, 234), but in neither of these investigations was any derivative of cupric iodide obtained.

By operating in aqueous solutions, *diaquobisethylenediamminocupric iodide* (I) has now been prepared as a well-defined crystalline substance quite stable in air. When left over sulphuric acid, this salt loses half its combined water and passes into *monoaquobisethylenediamminocupric iodide* (II), which undergoes no further change in dry air even up to 110°, although in a moist atmosphere it reverts to the dihydrate.

$$\text{(I.)}\ [2H_2O,Cu,2en]I_2 \rightleftharpoons [H_2O,Cu,2en]I_2\ \text{(II.)}$$

The dehydration is accompanied by a change of colour from deep purple to lilac or mauve. This monohydrate corresponds in type with the methyl alcoholate $[CH_4O,Cu,2en]I_2$ and alcoholate $[C_2H_6O,Cu,2en]I_2$ described on pp. 2023, 2028.

Comparative experiments on the chloride and bromide $[Cu,2en,2H_2O]X_2$ showed that these salts are not converted into monohydrates when left over sulphuric acid.

II. *Amminated Cupric Cuprocyanides.*

The co-ordination theory affords a simple explanation of the chemical constitutions of complex copper cyanides, including their combinations with alkali cyanides and with ammonia. This clue to the structure of these copper compounds is based on the view that cuprous cyanide itself is a highly associated molecule, $[Cu_x(CN)_x]$, which becomes more or less depolymerised when combining with alkali cyanides to form such soluble double cyanides as $K[Cu_2(CN)_3]$ and $K[Cu(CN)_2]$. These alkali derivatives are salts of hypothetical dicuprocyanic and cuprocyanic acids, $HCu_2(CN)_3$ and $HCu(CN)_2$, belonging to a series containing the minimum proportion of cation (meta-acids and salts). Other alkali salts containing a larger proportion of cation are known such as $K_2[Cu(CN)_3]$, $K_3[Cu(CN)_4]$ and $Rb_2[Cu_3(CN)_5]$. Complex derivatives of the hypothetical acids $H_2Cu(CN)_3$, $H_3Cu(CN)_4$, and $H_2Cu_6(CN)_5$ are classified below.

1. *Derivatives of* $H[Cu_2(CN)_3]$. The olive-yellow cupric dicuprocyanide, $Cu^{II}[Cu_2(CN)_3]_2,H_2O$, and its ammines fall into this group. Of the latter, the following have been isolated: The diammine, $[Cu,2NH_3,H_2O][Cu_2(CN)_3]_2$ (Monthiers, *J. Pharm.*, 1847, **11**, 257), and the anhydrous compound (Treadwell and Girsewald, *Z. anorg. Chem.*, 1904, **39**, 87); the tetrammine, $[Cu,4NH_3][Cu_2(CN)_3]_2$, and its dihydrate (Hilkenkamp, *Annalen*, 1856, **97**, 221); *pentamminocupric dicuprocyanide*, $[Cu,5NH_3][Cu_2(CN)_3]_2$, obtained in insoluble green scales by one of us (G. T. M.) and J. W. Porter (unpublished research, 1914) by adding to concentrated ammoniacal copper

sulphate half the amount of 15% aqueous potassium cyanide required to decolorise the solution *; the hexammine,

$$[Cu,6NH_3][Cu_2(CN)_3]_2,$$

prepared by Schiff and Bechi (*Compt. rend.*, 1865, **60**, 33).

It has now been found that ethylenediamine furnishes a very stable derivative of this series, namely, *bisethylenediamminocupric dicuprocyanide*, $[Cu,2en][Cu_2(CN)_3]_2$, obtained in pink crystals which differ markedly in colour from both the blue anhydrous tetrammine and its green dihydrate.

2. *Derivatives of* $H[Cu(CN)_2]$. The siskin-green cupric cuprocyanide, $Cu[Cu(CN)_2]_2$, and a numerous series of ammines containing two, three, four, and six molecular proportions of ammonia: the blue hexammine, $[Cu,6NH_3][Cu(CN)_2]_2$, readily dissociating into the green tetrammine, $[Cu,4NH_3][Cu(CN)_2]_2$. Similar compounds have been obtained from mono-, di-, and tri-methylamines, while pyridine furnishes complexes containing 2, 3, and 5 molecules of the base.

A stable *monoaquobisethylenediamminocupric cuprocyanide*, $[Cu,2en,H_2O][Cu(CN)_2]_2$, crystallising in well-defined, dark purple needles has now been obtained by several methods of preparation which leave no doubt as to its constitution. It loses its characteristic colour on dehydration, but the brown anhydrous compound regains the molecular proportion of water on exposure to the atmosphere.

3. *Derivatives of* $H_2[Cu(CN)_3]$. Although the cupric salt of this acid has not been identified, yet two ammines have been described: $[Cu,2NH_3,H_2O][Cu(CN)_3]$ and $[Cu_2,2NH_3,3H_2O][Cu(CN)_3]_2$ (Bouveault, *Bull. Soc. chim.*, 1890, **4**, 640; Fleurent, *Compt. rend.*, 1892, **114**, 1060).

The analogous product with ethylenediamine has the composition $2Cu(CN)_2,Cu_2(CN)_2,2en,H_2O$ and may be regarded as *monoaquobisethylenediamminodicupric cuprocyanide*,

$$[en{\cdot\cdot}Cu{\cdot\cdot}H_2O{\cdot\cdot}Cu{\cdot\cdot}en][Cu(CN)_3]_2.$$

The water present is held very tenaciously and is only partly eliminated after prolonged heating at 110°.

This ethylenediamine derivative, which contains equal atomic proportions of univalent and bivalent copper, represents probably the extent to which the diamine stabilises cupric cyanide. It is significant that both ammonia and ethylenediamine stop short of complete stabilisation at the same stage.

4. *Derivatives of* $H_2[Cu_3(CN)_5]$. The rubidium, cæsium, and calcium salts of this hypothetical acid have been described (Gross-

* Found: Cu, 56·5; NH_3, 15·3; CN, 28·9. $C_6H_{15}N_{11}Cu_5$ requires Cu, 56·9; NH_3, 15·2; CN, 27·9%.

mann and Van der Forst, *Z. anorg. Chem.*, 1905, **43**, 94) and we have now prepared the corresponding salt of ethylenediamine (III), obtaining it in both hemihydrated and anhydrous forms.

(III.) $\begin{bmatrix} CH_2{\cdot}NH_3 \\ CH_2{\cdot}NH_3 \end{bmatrix}[Cu_3(CN)_5]$ $\qquad$ $\begin{bmatrix} CH_2{\cdot}NH_3 \\ CH_2{\cdot}NH_3 \end{bmatrix}[CuX_2]_2$ (IV.)

The alkali salts of cuprochloric acid exhibit similar complications in regard to the anion as, for example, in $(NH_4)_2Cu_3Cl_5$ and $Cs_3Cu_2Cl_5$, but on combining ethylenediamine with cuprous chloride and bromide in the presence of the respective halogen hydride *ethylenediammonium cuprochloride* and *cuprobromide* of the simplest type (IV) were isolated, the latter being much the more stable of the two salts.

Co-ordination Numbers of Bivalent Copper.

In the preceding communication of this series (this vol., p. 914) it was pointed out that, owing to the electronic structure of the metallic radical, a co-ordination number 5 should be characteristic of bivalent copper, and the present investigation supplies further evidence on this point.

A survey of the extremely varied types of co-ordination compounds presented by copper suggests the operation of two opposing sets of forces. One set of forces, partly or wholly external to the copper atom, tends to marshal the associating units into symmetrical positions in the co-ordination complex so that, when these forces preponderate, co-ordination numbers of 4 and 6 are manifested. But to these forces making for symmetry is opposed another set arising from within the copper atom and depending upon the number and orientation of its chemically effective electrons. When these forces prevail, less symmetrical aggregates are produced and among such the system containing five associating units is predominant.

During this investigation two new co-ordinated cupric salts have been obtained: *tetra-aquoethylenediamminocupric perchlorate*, $[Cu,en,4H_2O](ClO_4)_2$, and a complex cupric cyanate,

$$Cu(CNO)_2,2en,2CH_3{\cdot}OH,4H_2O,$$

which on account of its excessive solubility in water only crystallises on addition of methyl alcohol. On the assumption that its organic addenda are associated with the metallic atom, this salt may be formulated as $[Cu,2en,2CH_3{\cdot}OH](CNO,2H_2O)_2$.

The foregoing perchlorate * and cyanate together with the

* Cupric perchlorate has also been combined with the following addenda: $4H_2O$, $2Cu(OH)_2$, $8NH_3$, $4NH_3$, $3NH_3 + H_2O$, $Cu(OH)_2 + 6NH_3 + 2H_2O$, and $Cu(OH)_2 + 4NH_3 + 2H_2O$ (Salvadori, *Gazzetta*, 1912, **42**, i, 458); $Cu(ClO_4)_2,4NH_3,2H_2O$, having been previously described by Roscoe (*Annalen*, 1862, **121**, 355).

most highly amminated iodides, $[Cu,6NH_3]I_2$, and cuprocyanides, $[Cu,6NH_3][Cu(CN)_2]_2$ and $[Cu,6NH_3][Cu_2(CN)_3]_2$, represent the symmetrical octahedral arrangement, but these hexammines are easily decomposed even at the ordinary temperature into penta- and tetra-ammines. Compounds exhibiting a co-ordination value of 5 such as $[Cu,4NH_3,H_2O]I_2$ and $[Cu,2en,H_2O][Cu(CN)_2]_2$ are more stable, but there is also a tendency to furnish the lower symmetrical arrangement of four associating units as in $[Cu,2en][Cu_2(CN)_3]_2$, which separates in this anhydrous form from aqueous solutions.

Moreover, the opposing tendencies are plainly seen on considering the bisethylenediamminocupric halides $[Cu,2en,2H_2O]X_2$. The chloride and bromide persist in the symmetrical dihydrated form whereas the iodide, although obtainable in this condition, passes readily into a monohydrate, monoalcoholate, and monomethyl-alcoholate, these three derivatives demonstrating a descent from 6 to 5 in the co-ordination number.

Experimental.

I. *Ethylenediammino-derivatives of Cupric Iodide.*

Cuprous iodide (1 mol. Cu_2I_2) and ethylenediamine (2 mols.) were shaken together in water containing a small amount of iodine. An intense violet coloration was developed immediately, although but little cuprous iodide dissolved. The mixture was heated to 60° while air was bubbled through it; the cuprous salt then passed into solution with the deposition of an orange-brown precipitate containing cuprous hydroxide and copper. The filtered solution was concentrated until intensely purple, tabular crystals slowly separated. On recrystallisation from water the purple salt was obtained in large, compact, prismatic crystals which, when dried on a porous plate and subsequently over anhydrous calcium chloride, retained their colour (Found: Cu, 13·6; I, 53·9; C, 10·0; H, 4·2; N, 12·0. $C_4H_{20}O_2N_4I_2Cu$ requires Cu, 13·4; I, 53·6; C, 10·1; H, 4·25; N, 11·8%). These numbers indicate the *dihydrate*. *Diaquobisethylenediamminocupric iodide* (I) was extremely soluble in water, sparingly so in methyl alcohol and insoluble in ether, acetone, benzene, or chloroform. In aqueous solution it was unaffected by caustic soda or potassium iodide, even on warming, but with cold silver nitrate, a quantitative precipitation of silver iodide occurred, thus indicating that the iodine was entirely ionised in an aqueous solution of the cupric salt.

On heating, this complex iodide darkened at 90° and melted with decomposition at 240° to a green liquid. In moist air the dihydrate was somewhat hygroscopic, but when left over concentrated sulphuric acid it lost half its water in 48 hours and thereafter

the residue remained of constant weight (Found : H_2O, 3·7. Calc. for one H_2O, 3·8%). This partial dehydration was accompanied by a change of colour from deep purple to pale mauve or lilac.

The *monohydrate* (II), which resembled the dihydrate in its chemical reactions, gave the following data : Cu, 14·0; I, 55·9; C, 10·5; H, 4·1; N, 12·5. $C_4H_{18}ON_4I_2Cu$ requires Cu, 13·95; I, 55·7; C, 10·5; H, 4·0; N, 12·3%).

Monoaquobisethylenediamminocupric iodide (II) is quite stable in a stoppered bottle or at 110°, but on exposure to moist air it reverts quantitatively to the dihydrate.

Methanolbisethylenediamminocupric Iodide $[CH_3{\cdot}OH,Cu,2en]I_2$.—On adding excess of pure methyl alcohol to a concentrated aqueous solution of hydrated bisethylenediamminocupric iodide bluish-purple glistening leaflets separated. These were purified by redissolution in water with addition of more methyl alcohol (Found : C, 12·65; H, 4·2; N, 12·0; I, 53·9; Cu, 13·65. $C_5H_{20}ON_4I_2Cu$ requires C, 12·8; H, 4·3; N, 11·9; I, 54·0; Cu, 13·5%). This cupric iodide derivative was very soluble in water, sparingly so in methyl or ethyl alcohol, and insoluble in ether or non-hydroxylic solvents. Blackening occurred at 100° and melting with decomposition to a blue liquid at 225—230°.

II. *Ethylenediammino-derivatives of Cupric Cuprocyanides.*

Monoaquobisethylenediamminocupric Cuprocyanide, $[Cu,2en,H_2O][Cu(CN)_2]_2$.—To the dark blue solution containing copper sulphate (1 mol.) and ethylenediamine (2 mols.) was added half the amount of 10% aqueous potassium cyanide required for complete decolorisation. The liquid was concentrated and allowed to cool; lustrous, deep purple needles then separated. Further evaporation produced another crop of these crystals, which dissolve only sparingly in cold water, are more soluble in warm water but insoluble in alcohol and other organic media (Found : Cu, 43·8; C, 22·2; H, 4·2; N, 26·2; CN, 23·2. $C_8H_{18}ON_8Cu_3$ requires Cu, 44·1; C, 22·2; H, 4·2; N, 25·9; CN, 24·0%).

This complex monocuprocyanide was also obtained by the two following methods : (1) As the main product, separating in well-defined, dark purple needles, in the double decomposition between barium cyanide and bisethylenediamminocupric sulphate in aqueous solution (Found : Cu, 43·8; N, 26·2%). (2) An aqueous solution of potassium cuprocyanide, $KCu(CN)_2$, prepared by decomposing the siskin-green, cupric cuprocyanide, $Cu[Cu(CN)_2]_2$, with the calculated amount of potassium hydroxide, was added to bisethylenediamminocupric sulphate; a portion of the product then

separated immediately as a pale mauve, microcrystalline powder and a further crop crystallised in dark purple needles on concentrating the mother-liquor (Found: Cu, 43·9; N, 26·0%). On heating to 110°, the purple monohydrated cuprocyanide lost its water and passed into brown bisethylenediamminocupric cuprocyanide, $[Cu,2en][Cu(CN)_2]_2$ (Found: Cu, 45·7; loss, 4·1. Calc.: Cu, 45·9; 1 mol. H_2O, 4·2%). The anhydrous salt reverted to the purple monohydrate on exposure to moist air. On heating to 210—240° the brown compound melted with decomposition to a red liquid.

The purple cuprocyanide dissolved to a colourless solution in aqueous potassium cyanide, and when warmed with water or aqueous caustic soda this salt dissolved respectively to a purple or a deep blue solution from which, on rapid cooling, the following dicuprocyanide separated as a pink, crystalline precipitate.

Bisethylenediamminocupric Dicuprocyanide, $[Cu,2en][Cu_2(CN)_3]_2$.—In addition to the foregoing mode of formation, this dicuprocyanide was prepared by the following reactions: (1) Double decomposition between bisethylenediamminocupric sulphate and a solution of potassium dicuprocyanide, $KCu_2(CN)_3$, prepared by warming aqueous potassium cyanide with excess of cuprous cyanide (Found: Cu, 53·3; N, 24·0%). (2) Freshly precipitated cuprous cyanide was boiled with excess of aqueous ethylenediamine and hydrocyanic acid; the cyanide dissolved to a purple solution from which the complex dicuprocyanide separated as a pink, crystalline precipitate (Found: Cu, 53·5; C, 19·7, 19·6; H, 2·85, 2·9; N, 23·95; CN, 25·8. $C_{10}H_{16}N_{10}Cu_5$ requires Cu, 53·5; C, 20·2; H, 2·7; N, 23·6; CN, 26·25%).

The dicuprocyanide darkened at 200° and decomposed at 240°, giving a red liquid; it was insoluble in water or organic media but dissolved in aqueous sodium cyanide to a colourless solution. When warmed with aqueous caustic soda, it dissolved to a blue solution from which the original pink precipitate separated on cooling.

Monoaquobisethylenediamminodicupric Cuprocyanide, $[en{\cdot\cdot}Cu{\cdot\cdot}OH_2{\cdot\cdot}Cu{\cdot\cdot}en][Cu(CN)_3]_2$.—To a 20% solution of cupric sulphate (1 mol.) and ethylenediamine (1 mol.) was added half the amount of 10% aqueous potassium cyanide required for complete decolorisation; a dull bluish-green, microcrystalline precipitate then separated which was insoluble in water or alcohol but dissolved in aqueous caustic soda to a blue solution from which black cupric oxide was precipitated on boiling. With sodium cyanide the compound dissolved to a blue solution which became colourless on warming (Found: Cu,

46·7; C, 21·7; H, 3·35; N, 25·25; CN, 27·8. $C_{10}H_{13}ON_{10}Cu_4$ requires Cu, 46·35; C, 21·9; H, 3·3; N, 25·5; CN, 28·4%). On heating at 110° for several hours, the compound lost only 80% of its contained water.

This substance was also produced by the following methods: (1) On adding bisethylenediamminocupric sulphate to a warm solution of potassium cuprocyanide, $KCu(CN)_2$, containing hydrocyanic acid (Found: Cu, 46·9; C, 21·5; H, 3·2; N, 25·4%). (2) When purple aquobisethylenediamminocupric cuprocyanide was warmed with aqueous hydrogen cyanide, these crystals assumed a green tint.

The Compound $C_{25}H_{80}O_6N_{24}Cu_5$.—Freshly prepared cuprous cyanide was mixed with strong hydrocyanic acid, and ethylenediamine was added with stirring until the cuprous compound had dissolved. The solution, which had warmed appreciably on the addition of the diamine, was cooled and filtered. The dark blue, oily filtrate, after evaporation to a small bulk on the water-bath, was left for some days in a desiccator. Compact, prismatic, saxe-blue crystals separated very slowly and were dried over sulphuric acid (Found: Cu, 28·1; C, 26·5; H, 7·1; N, 29·7; CN, 13·6. $C_{25}H_{80}O_6N_{24}Cu_5$ requires Cu, 28·1; C, 26·5; H, 7·1; N, 29·7; CN, 13·8%). These data correspond with the formula

$$Cu_5(CN)_6,9C_2H_4(NH_2)_2,H_2CO_3,3H_2O,$$

carbon dioxide having been slowly absorbed from the atmosphere. The substance was decomposed on prolonged exposure to air with formation of more highly carbonated products. It dissolved readily in water or alcohol, but not in ether, chloroform or benzene. It darkened at 70° and melted at 125° to a deep blue liquid. Not affected by aqueous alkalis, it was decolorised by alkali cyanide. Mineral acids precipitated cuprous cyanide with evolution of hydrogen cyanide. Its aqueous solution reduced silver nitrate but not Fehling's solution.

III. *Ethylenediammonium Cupro-salts.*

Ethylenediammonium Tricuprocyanide Hemihydrate (III).—Freshly precipitated cuprous cyanide and copper foil were boiled with an aqueous solution of ethylenediamine containing excess of hydrocyanic acid. The filtrate, from which a pink precipitate of dicuprocyanide separated, was again boiled with excess of hydrocyanic acid to insure a colourless solution. On cooling, small glistening plates of the tricuprocyanide separated (Found: Cu, 48·8; C, 21·4; H, 3·1; N, 25·25; CN, 31·9. $C_{14}H_{22}ON_{14}Cu_6$ requires Cu, 48·8; C, 21·5; H, 2·6; N, 25·1; CN, 33·3%). When quite dry, this tricuprocyanide was stable in air, but was readily decom-

posed by water, yielding cuprous cyanide. It was insoluble in all organic media, darkened on heating at 100° and decomposed at 240°. When maintained at 110°, the salt loses its combined water (Found: loss, 2·3. Calc. for $\frac{1}{2}H_2O$: loss, 2·3%. Found: Cu in residue, 50·2. $C_7H_{10}N_7Cu_3$ requires Cu, 49·95%).

Ethylenediammonium Cuprochloride (IV).—Freshly prepared uprous chloride (3·9 g.) was digested with excess of hydrochloric acid, ethylenediamine (2·3 g.), and copper foil, the mixture being boiled in a stream of carbon dioxide until the solution was colourless. On cooling, large colourless plates of the cuprochloride were deposited; these were recrystallised from hot dilute hydrochloric acid (Found: Cu, 38·3; C, 7·1; H, 3·0; N, 9·0; Cl, 42·5. $C_2H_{10}N_2Cl_4Cu_2$ requires Cu, 38·4; C, 7·2; H, 3·0; N, 8·5; Cl, 42·8%). When quite dry, the cuprochloride was stable, but with a trace of moisture it rapidly oxidised in air, becoming yellow and then green. The compound blackened at 120° and decomposed at 210° into a black liquid. It was dissociated by water in the cold into its component chlorides; boiling aqueous caustic alkalis gave cuprous oxide.

Ethylenediammonium cuprobromide (IV), prepared in a similar manner to the cuprochloride, crystallised from hydrobromic acid in long, colourless lamellæ (Found: Cu, 25·1; C, 4·8; H, 1·6; N, 5·8; Br, 62·8. $C_2H_{10}N_2Br_4Cu_2$ requires Cu, 25·0; C, 4·7; H, 2·0; N, 5·5; Br, 62·8%). The cuprobromide was much less readily oxidised than the cuprochloride; it melted with slight blackening at 235°.

IV. *Tetra-aquoethylenediamminocupric Perchlorate*, $[Cu,en,4H_2O][ClO_4]_2$.

We are indebted to Dr. G. R. Davies for the preparation of the perchlorate obtained by concentrating an aqueous solution of cupric perchlorate and ethylenediamine in molecular proportions. The salt crystallised in dark bluish-violet needles (Found: Cu, 16·4; ClO_4, 49·8; en, 15·8. $C_2H_{16}O_{12}N_2Cl_2Cu$ requires Cu, 16·1; ClO_4, 50·4; en, 15·2%).

This perchlorate, although slightly hygroscopic, was stable in air at the ordinary temperature. About 0·8 g., heated in a porcelain crucible over a Méker burner, decomposed quietly, but in an attempt to burn 0·2 g. in oxygen for the determination of carbon and hydrogen the substance exploded with extreme violence. A similar quantity mixed with copper oxide and heated in carbon dioxide for a nitrogen estimation exploded vigorously.

The perchlorate was readily soluble in water to a dark purple solution, but practically insoluble in alcohol and other organic

media. Aqueous caustic soda gave a blue solution stable even on boiling, whereas the alcoholic alkali decomposed the salt, yielding cupric oxide.

V. *Ethylenediammino-derivative of Cupric Cyanate.*

A concentrated aqueous solution of potassium cyanate was added to a saturated solution of copper sulphate or acetate. The light green precipitate, after being washed successively with aqueous potassium cyanate and alcohol, was added to an aqueous solution of ethylenediamine until no more of the insoluble cyanate dissolved. The deep purple solution was evaporated to dryness over sulphuric acid, potassium cyanate being separated from time to time. The final residue was dissolved in hot methyl alcohol; the solution on evaporation deposited acicular crystals (Found: Cu, 15·7; C, 24·0; H, 7·6; en, 29·3. $C_8H_{32}O_8N_6Cu$ requires Cu, 15·7; C, 23·8; H, 8·0; en, 29·7%). This result corresponds with the composition of *bismethanolbisethylenediamminocupric cyanate tetrahydrate*, $[Cu,2en,2CH_3{\cdot}OH](CNO)_2,4H_2O$.

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[*Received, June 11th*, 1926.]

CCLXXI.—*Researches on Residual Affinity and Co-ordination. Part XXVIII. Thermal Measurements on Derivatives of Cupric Iodide.*

By GILBERT T. MORGAN, SYDNEY RAYMOND CARTER, and WILLIAM FINNEMORE HARRISON.

IT is well known that cupric iodide is extremely unstable and attempts to prepare it in aqueous solution usually result in the formation of cuprous iodide and free iodine.

On the other hand, cupric bromide and cupric chloride are comparatively stable and the affinity between the cuprous halide and free halogen in solution is represented relatively by the heats of reaction given by Thomsen ("Thermochemische Untersuchungen," iii, p. 319) in which the reaction between cuprous iodide and iodine is decidedly endothermic:

$$CuCl + Cl + aq. \longrightarrow CuCl_2aq. + 29{\cdot}83 \text{ Cals.}$$
$$CuBr + Br + aq. \longrightarrow CuBr_2aq. + 15{\cdot}84 \text{ Cals.}$$
$$CuI + I + aq. \longrightarrow CuI_2aq. - 5{\cdot}85 \text{ Cals.}$$

It is, therefore, of interest to compare these values with the heats

of chelation of ethanolbisethylenediamminocupric iodide which is also in aqueous solution.

$$CuI + I + 2en\ aq. + C_2H_6O = [Cu,2en,C_2H_6O]I_2aq. + 22{\cdot}12\ Cals.$$

The formation of the co-ordination compound of cupric iodide from its generators, cuprous iodide, free iodine, alcohol, and aqueous ethylenediamine, proceeds with a positive heat evolution (+ 22·12 Cals.) which is intermediate between that required for the formation of the simple cupric chloride (+ 29·83 Cals.) and cupric bromide (+ 15·84 Cals.) from the corresponding halogens and cuprous halides respectively.

The formation of the monoalcoholate is accompanied by practically the same quantity of heat as that observed in the formation of the corresponding hydrates in which the elements of alcohol are replaced by those of water.

The close agreement in the heats of formation of the monoalcoholate (+ 55·28 Cals.), monohydrate (+ 53·78 Cals.) and of the dihydrate (+ 55·55 Cals.) is noteworthy and in the case of the hydrated salts is in accordance with the fact that the dihydrate can be readily transformed into the monohydrate by gentle desiccation.

Experimental.

The preparation described below was carried out before the isolation of the hydrated forms of bisethylenediamminocupric iodide recorded in the preceding paper.

Ethanolbisethylenediamminocupric Iodide, $[Cu,2en,C_2H_6O]I_2$.—On passing air through a suspension of freshly precipitated cuprous iodide in water at 60° containing the calculated amount of ethylenediamine, an intense bluish-violet solution was produced, the iodide dissolving while a brown precipitate containing cuprous hydroxide and copper was deposited. Addition of iodine facilitated the solution of the cuprous iodide. After the greater part of the substance had dissolved, the filtered solution was concentrated to a small volume, cooled in ice and salt, and treated with alcohol; dark bluish-purple, glistening plates then separated. This product, recrystallised by the addition of alcohol to its saturated aqueous solution, was dried in a vacuum desiccator (Found: C, 14·5, 14·5; H, 5·2, 5·1; N, 12·0; Cu, 13·25; I, 52·8; $C_2H_8N_2$, 25·2. $C_6H_{22}ON_4I_2Cu$ requires C, 14·9; H, 4·55; N, 11·6; Cu, 13·15; I, 52·5; $C_2H_8N_2$, 24·8%).

The monoalcoholate, although stable in air, has a faint but appreciable odour of iodoform due to a slight interaction of the iodine and alcohol present in its molecule. On heating, the crystals darkened at 100° and melted with decomposition to a deep blue

liquid at 235°. Extremely soluble in water, the compound dissolved less freely in methyl or ethyl alcohol; it was only slightly soluble in ether and insoluble in benzene, acetone, or chloroform. The aqueous solution was unaffected by sodium hydroxide or potassium iodide, whereas with silver nitrate it gave a copious precipitate of silver iodide.

Thermal Measurements.

A thin-walled glass beaker was used for the calorimeter, since the aqueous solution attacked both nickel and silver. The dry, finely divided compounds could not be added directly to the hydrochloric acid solution, since the powder tended to conglomerate into lumps which were not entirely decomposed. Consequently the compound was first dissolved in water and the solution then acted upon by the acid.

Ethanolbisethylenediamminocupric Iodide, $[Cu,2en,C_2H_6O]I_2$.—The heat of dissociation of this compound was determined by adding 200 c.c. of *N*-hydrochloric acid to 3 g. of the compound dissolved in 200 c.c. of water and observing the temperature change, the additive compound being decomposed with formation of cuprous iodide and free iodine. The heat of dissociation found was + 24·96 Cals., whilst the heat of solution of the compound in water (1 : 70) was − 12·41 Cals. Thomsen (*op. cit.*, p. 319) gives the following data :

$[Cu_2,I_2] = +32{\cdot}52$ Cals. and $[Cu,I_2,aq.] = +10{\cdot}41$ Cals.

Hence $CuI + I + aq. \longrightarrow CuI_2aq. - 5{\cdot}85$ Cals.

The heat of neutralisation of ethylenediamine in aqueous solution by two molecules of hydrochloric acid is + 23·54 Cals. (Colson and Darzens, *Compt. rend.*, 1894, **118**, 250). The heat of solution of anhydrous ethylenediamine (1 : 65) is + 7·45 Cals. and the heat of solution of ethylenediamine monohydrate (1 : 65) is + 4·68 Cals. (Berthelot, *Ann. Chim.*, 1900, **20**, 163).

$[Cu,2en,C_2H_6O]I_2aq. + 4HCl \longrightarrow CuI + I + 2C_2H_8N_2,2HClaq. + C_2H_6O + 24{\cdot}96$ Cals.

$2C_2H_8N_2aq. + 4HCl \longrightarrow 2C_2H_8N_2,2HClaq. + 47{\cdot}08$ Cals.

Hence $CuI + I + C_2H_6O + 2C_2H_8N_2aq. \longrightarrow [Cu,2en,C_2H_6O]I_2aq. + 22{\cdot}12$ Cals.

or $CuI_2aq. + C_2H_6O + 2C_2H_8N_2aq. \longrightarrow [Cu,2en,C_2H_6O]I_2aq. + 27{\cdot}97$ Cals.

Correcting for the heats of solution of ethylenediamine and the additive compound in water, a value of + 55·28 Cals. is obtained for the heat of reaction of cupric iodide and two molecules of ethylenediamine.

Monoaquobisethylenediamminocupric Iodide, $[Cu,2en,H_2O]I_2$.—By adopting the foregoing method, the heat of solution in water (1 : 100) was found to be — 9·55 Cals. and the heat of dissociation by 0·5 *N*-hydrochloric acid was + 23·60 Cals. This gives a heat of reaction of + 53·78 Cals.

Diaquobisethylenediamminocupric Iodide, $[Cu,2en,2H_2O]I_2$.—The heat of solution in water (1 : 100) was — 11·82 Cals., whilst the heat of dissociation by 0·5 *N*-hydrochloric acid was + 24·10 Cals., which gives a value of + 55·55 Cals. for the heat of reaction of ethylenediamine with cupric iodide in forming the above compound.

The authors desire to express their thanks to the Advisory Council of the Department of Scientific and Industrial Research for a grant which has partly defrayed the expense of this investigation.

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[*Received, June 11th*, 1926.]

CCLXXII.—*Nitration of Chlorinated 3-Hydroxybenzaldehydes and some Consequences of Adjacent Substitution.*

By HERBERT HENRY HODGSON and HERBERT GREENSMITH BEARD.

THE literature of this subject describes only the 6-chloro-3-hydroxy-2- and -4-nitrobenzaldehydes (Friedländer and Schenk, *Ber.*, 1914, **47**, 3044).

The present investigation has revealed the potent influence of chlorine in position 2 on adjacent groups; *e.g.*, by comparing the volatility in steam of 6-nitro-3-hydroxybenzaldehyde (non-volatile), 6-nitro-3-methoxybenzaldehyde (volatile), and 2-chloro-6-nitro-3-methoxybenzaldehyde (non-volatile) and of 4-nitro-3-hydroxybenzaldehyde (volatile), 4-nitro-3-methoxybenzaldehyde (non-volatile), and 2-chloro-4-nitro-3-methoxybenzaldehyde (volatile), it is seen that the methoxy-group has been made to function as a phenolic hydroxyl group, for the former chloro-compound displays the non-volatility of a *p*-nitrophenol, and the latter the ready volatility of an *o*-nitrophenol. Again, the nitration of 2-chloro-3-methoxybenzaldehyde gives a mixture of 2-chloro-3-methoxy-4- and -6-nitrobenzaldehydes only, whereas from Rubinstein's work (J., 1925, **127**, 2268) the formation of 2-chloro-5-nitro-3-methoxybenzaldehyde might have been expected.

On treatment with aqueous sodium hydroxide, 6-chloro-2 : 4-dinitro-3-hydroxybenzaldehyde-*p*-nitrophenylhydrazone develops a vivid royal-blue colour, whilst 2-chloro-4 : 6-dinitro-3-hydroxybenzaldehyde-*p*-nitrophenylhydrazone gives a claret colour only on warming, and then but slowly, thereby differing from all other *p*-nitrophenylhydrazones which have been examined. The behaviour of the latter recalls that of 2 : 5-dichloro-6-nitrobenzaldehydephenylhydrazone, which was the only exception to Chattaway and Clemo's generalisation (J., 1923, **123**, 3043); in both cases the anomalous behaviour may be connected with the presence of a chlorine atom in position 2.

Chlorinated 4-nitro-3-hydroxybenzaldehydes are in general sparingly soluble in water and readily soluble in non-hydroxylic solvents (benzene, chloroform, etc.). The reverse holds for the 6-nitro-isomerides.

The constitutions of the chloronitro-3-hydroxybenzaldehydes have been established by further nitration: 2-chloro-3-hydroxy-4- and -6-nitrobenzaldehydes give the same dinitro-compound, 2-chloro-4 : 6-dinitro-3-hydroxybenzaldehyde; 4-chloro-3-hydroxy-2- and -6-nitrobenzaldehydes give 4-chloro-2 : 6-dinitro-3-hydroxybenzaldehyde; and 6-chloro-3-hydroxy-2- and -4-nitrobenzaldehydes give 6-chloro-2 : 4-dinitro-3-hydroxybenzaldehyde.

By working with a much larger quantity of material, we have been able to show that 2 : 6-dichloro-3-hydroxybenzaldehyde is the main constituent of the mixture of dichloro-compounds produced by the chlorination of 6-chloro-3-hydroxybenzaldehyde (this vol., p. 152).

4-Chloro-2 : 6-dinitro-3-hydroxybenzaldehyde and its derivatives explode with much greater violence than the corresponding 2- and 6-chloro-isomerides; the silver salts are the most explosive derivatives. The 6-nitro-compounds, and even the silver salts when powdered, have pronounced sternutatory properties.

Experimental.

General Procedure.—The silver salts described below were prepared by treating the hydroxy-compounds, dissolved in the theoretical quantity of 1% aqueous ammonia, with the requisite quantities of 5% aqueous silver nitrate. These precautions were taken to prevent any possible displacement of chlorine from the various chloronitro-compounds investigated. On account of their highly explosive nature, the silver salts were analysed by warming them with dilute hydrochloric acid and washing the silver chloride with ether until its weight became constant.

The p-*nitrophenylhydrazones* were made by the authors' general

method (J., 1925, **127**, 880). The characteristic colour produced by addition of aqueous sodium hydroxide to an aqueous suspension of the hydrazone is given in brackets immediately after the m. p.

The oximes and methyl ethers were respectively obtained by the methods employed for the preparation of the oximes of the bromo-compounds (*loc. cit.*, p. 878) and the methyl ethers of the chloro-compounds (this vol., p. 153).

Mononitration of 2-Chloro-3-hydroxybenzaldehyde.

2-Chloro-3-hydroxybenzaldehyde (25 g.) dissolved in 50% aqueous acetic acid (70 c.c.) was nitrated at 45—55° by the gradual addition of nitric acid (25 c.c.; *d* 1·3). After 15 minutes, the mixture was cooled and poured on to ice (150 g.). The mixture of 2-chloro-3-hydroxy-4- and -6-nitrobenzaldehydes, obtained in quantitative yield, was treated with 600 c.c. of water at 90°, which dissolved the 6-nitro-compound and a little of the 4-nitro-isomeride; the latter was removed by steam distillation. The residue was almost pure 2-chloro-4-nitro-3-hydroxybenzaldehyde. The yields of the 4- and 6-nitro-compounds were 17 g. and 12 g., respectively.

2-Chloro-4-nitro-3-hydroxybenzaldehyde forms deep yellow needles, m. p. 166°, from glacial acetic acid (Found: Cl, 17·4. $C_7H_4O_4NCl$ requires Cl, 17·6%). The *silver* salt crystallises from hot water in red micro-needles (Found: Ag, 34·6. $C_7H_3O_4NClAg$ requires Ag, 35·0%). The p-*nitrophenylhydrazone* separates from hot glacial acetic acid, in which it is sparingly soluble, in deep orange needles, m. p. 294—295° (decomp.). (Violet.) (Found: Cl, 10·4. $C_{13}H_9O_5N_4Cl$ requires Cl, 10·5%.) The *semicarbazone* forms sulphur-yellow needles, m. p. 271—272° (decomp.), from hot alcohol (Found: Cl, 13·5. $C_8H_7O_4N_4Cl$ requires Cl, 13·7%). The *oxime*, which is insoluble in water, crystallises from hot alcohol in stout yellow needles, m. p. 170° (Found: Cl, 16·2. $C_7H_5O_4N_2Cl$ requires Cl, 16·4%).

2-Chloro-4-nitro-3-methoxybenzaldehyde crystallises from dilute acetic acid or dilute alcohol in colourless needles, m. p. 107° (Found: Cl, 16·4. $C_8H_6O_4NCl$ requires Cl, 16·5%).

2-Chloro-6-nitro-3-hydroxybenzaldehyde crystallises from water in colourless needles, m. p. 153° (Found: Cl, 17·6. $C_7H_4O_4NCl$ requires Cl, 17·6%). The *silver* salt forms cinnamon-brown needles from hot water, in which it is much more soluble, and the ammonium salt is much less soluble, than the corresponding 4-nitro-isomerides (Found: Ag, 34·6%). The p-*nitrophenylhydrazone* is obtained as a dull orange-red gelatinous substance which crystallises from hot dilute acetic acid in needles, m. p. 232—233°. (Claret.) (Found: Cl, 10·2%.) The *semicarbazone* forms pale yellow needles, m. p.

234° (decomp.), from alcohol (Found: Cl, 13·6%). The *oxime*, which is exceedingly soluble in alcohol and water, crystallises from chloroform in colourless needles, m. p. 175° (Found: Cl, 16·3%).

2-Chloro-6-nitro-3-methoxybenzaldehyde crystallises from glacial acetic acid in colourless needles, m. p. 134° (Found: Cl, 16·6%).

Preparation of 2-Chloro-3-methoxy-4- and -6-nitrobenzaldehydes by Direct Nitration.—2-Chloro-3-methoxybenzaldehyde (3 g.) dissolved in concentrated sulphuric acid (14 g.) was nitrated at 30—40° by the gradual addition of finely powdered potassium nitrate (2 g.); the mixture was kept for 10 minutes at 50—60° and then poured on to ice. The 2-chloro-4-nitro-3-methoxybenzaldehyde (m. p. 107°) was separated quantitatively from the 6-nitro-compound (m. p. 134°) by means of its volatility in steam.

Mononitration of 4-Chloro-3-hydroxybenzaldehyde.

4-Chloro-3-hydroxybenzaldehyde was conveniently obtained by the following modification of the method previously described (this vol., p. 150). 4-Nitro-3-hydroxybenzaldehyde (31 g.) suspended in water (500 c.c.) was reduced by sodium hyposulphite (140 g.), added as rapidly as the violence of the reaction permitted. The mixture was kept for 15 minutes at 90°, cooled to 0°, mixed with concentrated hydrochloric acid (100 c.c.), and diazotised below 5° with solid sodium nitrite (40 g.). Concentrated hydrochloric acid (50 c.c.) and sodium nitrite (15 g.) were then added, the mixture was kept for 30 minutes, and the free nitrous acid destroyed by carbamide. The diazo-solution was added slowly to a boiling mixture of cuprous chloride (40 g.), concentrated hydrochloric acid (100 c.c.), and water (100 c.c.), and the whole was boiled under reflux for 2 hours and finally extracted with benzene (600 c.c.) at about 70°, the bisulphite compound of the aldehyde being probably most dissociated at this temperature (compare Erhart, D.R.-P. 116124, on the separation of *o*- and *m*-nitrobenzaldehydes). The yield was 17 g. (60%) and the product, after crystallisation from 50% aqueous acetic acid, melted at 121°.

Nitration. This was effected as in the case of 2-chloro-3-hydroxybenzaldehyde. The mixture (4 g.) of 4-chloro-3-hydroxy-2- and -6-nitrobenzaldehydes obtained was boiled under reflux with chloroform (16 g.) for 30 minutes, cooled, and filtered. The residue (3·8 g.) was almost pure 4-chloro-6-nitro-3-hydroxybenzaldehyde, whilst the filtrate gave 0·2 g. of the 2-nitro-isomeride. Separation of these two by fractional steam distillation entailed serious loss.

4-Chloro-2-nitro-3-hydroxybenzaldehyde crystallises from glacial acetic acid in yellow needles, m. p. 161° (Found: Cl, 17·4. $C_7H_4O_4NCl$ requires Cl, 17·6%). The *silver* salt forms orange-red

needles from hot water (Found: Ag, 34·7%). The p-*nitrophenylhydrazone* forms deep red needles, m. p. 281—282° (decomp.), from hot glacial acetic acid. (Violet.) (Found: Cl, 10·4%.) The *semicarbazone* crystallises from dilute alcohol in pale yellow needles, m. p. 270—271° (decomp.) (Found: Cl, 13·6%).

4-*Chloro*-6-*nitro*-3-*hydroxybenzaldehyde* crystallises from glacial acetic acid in thick, colourless, elongated prisms, m. p. 175° (Found: Cl, 17·3. $C_7H_4O_4NCl$ requires Cl, 17·6%). The *silver* salt forms orange needles from hot water (Found: Ag, 34·8%). The p-*nitrophenylhydrazone* forms deep maroon needles, m. p. 275—276° (decomp.), from hot glacial acetic acid. (Reddish-violet.) (Found: Cl, 10·5%.) The *semicarbazone* crystallises from alcohol in light orange needles, m. p. 265—266° (decomp.) (Found: Cl, 13·5%).

Mononitration of 6-*Chloro*-3-*hydroxybenzaldehyde.*

Friedländer and Schenk's process (*loc. cit.*) was repeated and their results were confirmed.

6-Chloro-2-nitro-3-hydroxybenzaldehyde forms yellow needles, m. p. 136°, from dilute acetic acid (F. and S. give m. p. 138°). The *silver* salt crystallises in brick-red needles from hot water, in which it is readily soluble (Found: Ag, 34·8%). The p-*nitrophenylhydrazone* forms deep orange needles, m. p. 256—257° (decomp.), from dilute acetic acid. (Brilliant red.) (Found: Cl, 10·3%.) The *semicarbazone* forms yellow needles, m. p. 249—250° (decomp.), from alcohol (Found: Cl, 13·7%).

6-Chloro-3-hydroxy-4-nitrobenzaldehyde crystallises from glacial acetic acid in deep yellow needles, m. p. 104° (F. and S. give m. p. 104°). The *silver* salt forms brownish-purple leaflets from hot water, in which it is difficultly soluble (Found: Ag, 34·7%). The p-*nitrophenylhydrazone* crystallises from glacial acetic acid in deep brick-red needles, m. p. 284—286° (decomp.). (Violet.) (Found: Cl, 10·5%.) The *semicarbazone* forms yellow plates, m. p. 266—267° (decomp.), from hot alcohol, in which it is only slightly soluble (Found: Cl, 13·6%).

Mononitration of 2 : 4- *and* 2 : 6-*Dichloro*-3-*hydroxybenzaldehyde.*

Either compound (3 g.), dissolved in glacial acetic acid (12 c.c.), was nitrated at 65° with nitric acid (3 c.c.; *d* 1·42); the mixture was kept for 15 minutes and then worked up in the usual way.

2 : 4-*Dichloro*-6-*nitro*-3-*hydroxybenzaldehyde* separates in colourless needles, m. p. 107°, from its deep yellow solution in glacial acetic acid or hot water (Found: Cl, 29·7. $C_7H_3O_4NCl_2$ requires Cl, 30·0%). The *silver* salt is precipitated in pale yellow microneedles insoluble in hot or cold water (Found: Cl, 20·4.

$C_7H_2O_4NCl_2Ag$ requires Cl, 20·7%). The p-*nitrophenylhydrazone* crystallises from hot glacial acetic acid in orange needles, m. p. 279—280°. (Red.) (Found: Cl, 19·0. $C_{13}H_8O_5N_4Cl_2$ requires Cl, 19·1%.) The *semicarbazone* separates from dilute alcohol in yellow needles which soften at 140—150° and contain water (Found: Cl, 22·8. $C_8H_6O_4N_4Cl_2,H_2O$ requires Cl, 22·8%).

2 : 6-*Dichloro*-4-*nitro*-3-*hydroxybenzaldehyde* forms bright yellow needles from dilute acetic acid and plates from water; m. p. 80° (Found: Cl, 29·9%). It is very slowly volatile in steam. The *silver* salt crystallises in crimson needles from hot water (Found: Ag, 31·2. $C_7H_2O_4NCl_2Ag$ requires Ag, 31·4%). The p-*nitrophenylhydrazone* forms deep red needles, m. p. 279—280° (decomp.), from hot glacial acetic acid. (Claret.) (Found: Cl, 19·0%.) The *semicarbazone* separates from hot alcohol in light yellow leaflets, m. p. 255—256° (Found: Cl, 24·1. $C_8H_6O_4N_4Cl_2$ requires Cl, 24·2%). The *oxime* forms deep yellow needles, m. p. 195°, from dilute alcohol (Found: Cl, 28·2. $C_7H_4O_4N_2Cl_2$ requires Cl, 28·3%).

Dinitration of 2-, 4-, *and* 6-*Chloro*-3-*hydroxybenzaldehydes.*

The nitrations were carried out as in the preceding case. The 2-chloro-compound gave pure 2-chloro-4 : 6-dinitro-3-hydroxybenzaldehyde, but pure 4-chloro-2 : 6-dinitro-3-hydroxybenzaldehyde and pure 6-chloro-2 : 4-dinitro-3-hydroxybenzaldehyde were best obtained in two stages by way of the respective mononitro-compounds.

2-*Chloro*-4 : 6-*dinitro*-3-*hydroxybenzaldehyde* forms very pale yellow needles, m. p. 110°, from glacial acetic acid (Found: Cl, 14·5. $C_7H_3O_6N_2Cl$ requires Cl, 14·4%). The *ammonium* salt is only moderately easily soluble in water. The *silver* salt crystallises from water in bright orange needles, which are easily soluble in water, acetone, or alcohol. The p-*nitrophenylhydrazone* forms dark crimson needles, m. p. 277—279° (with explosive decomp.), from glacial acetic acid (Found: Cl, 9·2. $C_{13}H_8O_7N_5Cl$ requires Cl, 9·3%). The *semicarbazone* crystallises from dilute alcohol in yellow needles, m. p. 240—242° (decomp.) (Found: Cl, 11·4. $C_8H_6O_6N_5Cl$ requires Cl, 11·7%). The *oxime* forms pale yellow needles, m. p. 142°, from alcohol (Found: Cl, 13·4. $C_7H_4O_6N_3Cl$ requires Cl, 13·6%).

4-*Chloro*-2 : 6-*dinitro*-3-*hydroxybenzaldehyde* forms very pale yellow needles, m. p. 118—119°, from water (Found: Cl, 14·7%). The *silver* salt forms orange-yellow needles from water, in which it is very soluble. The p-*nitrophenylhydrazone* crystallises from dilute acetic acid in deep orange-red needles, which explode at 235—236°. (Claret.) (Found: Cl, 9·1%.) The *semicarbazone* separates from

hot dilute alcohol in stout, deep yellow needles, which explode at about 200° (Found : Cl, 11·6%).

6-*Chloro*-2 : 4-*dinitro*-3-*hydroxybenzaldehyde*. The dinitration product required three crystallisations from dilute acetic acid before it was obtained pure in bright yellow needles, m. p. 121·5° (Found : Cl, 14·2. $C_7H_3O_6N_2Cl$ requires Cl, 14·4%). The *silver* salt is a deep red substance which is very soluble in water. The p-*nitrophenylhydrazone* crystallises in dark crimson needles, m. p. 285—286° (decomp.), from glacial acetic acid (Found : Cl, 9·2%). The *semicarbazone* forms yellow needles, m. p. 267—269° (decomp.), from alcohol (Found : Cl, 11·5%).

We are greatly indebted to the Department of Scientific and Industrial Research and the North Riding Education Authority for grants to one of us (H. G. B.), and also to the British Dyestuffs Corporation for gifts of chemicals.

TECHNICAL COLLEGE, HUDDERSFIELD. [*Received, March 22nd*, 1926.]

CCLXXIII.—*Nitrosation of Phenols. Part III. Nitrosation of* 4-*Halogeno*-o- *and* -m-*cresols and Oximation of the* 4-*Halogeno*-2 : 5-*toluquinones.*

By HERBERT HENRY HODGSON and FRANCIS HARRY MOORE.

THE 5-nitroso-derivatives which have been obtained from 4-chloro-, 4-bromo-, and 4-iodo-*o*-cresol dissolve in aqueous sodium hydroxide without frothing and exist each in only one modification which preserves its identity whether crystallised from hot aqueous mineral acid or precipitated from alkaline solution (compare J., 1923, **123**, 2499; 1925, **127**, 2260). Since the m. p.'s of 3-chloro-4-nitrosophenol and 5-nitroso-*o*-cresol are 135° and 134—135°, respectively, whilst 4-chloro- and 4-bromo-5-nitroso-*o*-cresol both melt at 197°, our previous conclusions with regard to the relation between m. p. and constitution (*loc. cit.*, p. 2260) lead us to the opinion that the latter two compounds are quinoneoximes. Support for this view was found in the fact that in the case of the chloro- and bromo-compounds the substance produced by the nitrosation of the 4-halogeno-*m*-cresol was the same as that formed by the action of hydroxylamine hydrochloride on the 4-halogeno-2 : 5-toluquinone. No indication of stereoisomerism was observed—and this is remarkable, since Kehrmann, Tichvinsky, and Rüst (*Annalen*, 1898, **303**, 16) have described stereoisomeric 4-chloro-2 : 5-toluquinoneoximes, m. p. 170° and 165°, and stereoisomeric 4-bromo-2 : 5-toluquinone-

oximes, m. p. 186° and 178—180°. Our method of preparing the toluquinones—by the oxidation of 4-chloro- and 4-bromo-5-amino-*o*-cresol—ensured their purity, since any isomeric 4-chloro- and 4-bromo-6-amino-*m*-cresol present would have given the same toluquinones. It is significant that none of Kehrmann's 3-halogeno-2 : 5-toluquinones exhibits stereoisomerism.

The difficulties met with in the preparation of 2-iodo-4-nitrosophenol (*loc. cit.*, p. 2263) were again encountered in the nitrosation of 4-iodo-*m*-cresol. The final product decomposed at 170° (the iodonitroso-compounds do not melt), whereas the product of the oximation of 4-iodo-2 : 5-toluquinone decomposed at 181°; this difference is ascribed to the presence of impurities and not to isomerism.

In general, the m. p.'s of the halogenated compounds described in this paper decrease with increasing atomic weight of the halogen.

Experimental.

Preparation of the 4-*Halogeno*-o-*cresols.*—The 4-halogeno-2-nitrotoluene (⅓ g.-mol.) was reduced by a boiling solution of sodium sulphide (3 parts) in water (200 c.c.), and the 4-halogeno-*o*-toluidine distilled in steam. Concentrated sulphuric acid (75 c.c.) was added to the distillate, which was then evaporated until, on rapid cooling, it set to a paste of the crystalline sulphate. This was diazotised in the usual way, the excess of nitrous acid destroyed by carbamide, and the filtered solution decomposed by boiling dilute sulphuric acid through which a current of steam was passing; the 4-halogeno-*o*-cresols distilled in yields of about 75% calculated on the weight of the nitro-compound taken. They all crystallise from light petroleum in white needles.

4-Chloro-*o*-cresol has m. p. 73° (Auwers and Deines, *Zentr.*, 1924, II, No. 18, give m. p. 73—74°). 4-*Bromo*-o-*cresol* has m. p. 78° (Found: Br, 42·6. C_7H_7OBr requires Br, 42·8%), and 4-*iodo*-o-*cresol*, m. p. 65° (Found: I, 53·8. C_7H_7OI requires I, 54·2%).

Nitrosation of the 4-*Halogeno*-o-*cresols.*—The method used for the preparation of 3-chloro-4-nitrosophenol (J., 1923, **123**, 2502) was employed, the temperature being 0—10°. The product was filtered off after 12 hours and extracted with hot benzene to remove unchanged cresol (yield about 4 g. from 4 g. of 4-halogeno-*o*-cresol).

4-*Chloro*-5-*nitroso*-o-*cresol* crystallised from alcohol and from dilute hydrochloric acid in small, pale yellow, feathery needles, and from benzene in somewhat deeper yellow needles; m. p. 196°, 195°, and 197° (decomp.), respectively (Found: Cl, 20·5; N, 8·1; *M*, cryoscopic in phenol, 165. $C_7H_6O_2NCl$ requires Cl, 20·7; N,

8·2%; *M*, 171·5). The three samples appeared uniform under the microscope.

4-*Bromo*-5-*nitroso*-o-*cresol* crystallised from benzene, alcohol, and hot dilute hydrochloric acid in yellow, feathery needles, m. p. 197°, 197°, and 195° (decomp.), respectively (Found : Br, 36·9; N, 6·5; *M*, cryoscopic in phenol, 210. $C_7H_6O_2NBr$ requires Br, 37·0; N, 6·5%; *M*, 216).

4-*Iodo*-5-*nitroso*-o-*cresol* crystallised from aqueous alcohol and benzene in brown plates, m. p. 200° (decomp.) (Found : I, 48·0; N, 5·6; *M*, cryoscopic in phenol, 257. $C_7H_6O_2NI$ requires I, 48·3; N, 5·3%; *M*, 263).

In the Liebermann reaction the 4-halogeno-5-nitroso-*o*-cresols develop a deep green colour; this becomes greenish-brown when the solution is diluted and made alkaline.

Reduction of the 4-*Halogeno*-5-*nitroso*-o-*cresols to the* 4-*Halogeno*-5-*amino*-o-*cresols*.—To a solution of the nitroso-compound in aqueous sodium carbonate, solid sodium hyposulphite was added until the colour was discharged. The amine precipitated was crystallised from alcohol, 4-*chloro*-5-*amino*-o-*cresol*, m. p. 217° (Found : Cl, 22·5. C_7H_8ONCl requires Cl, 22·5%), 4-bromo-5-amino-*o*-cresol, m. p. 189° (Gattermann, *loc. cit.*, gives m. p. 180°) (Found : Br, 39·5. Calc. : Br, 39·6%), and 4-*iodo*-5-*amino*-o-*cresol*, m. p. 170° (Found : I, 51·4. C_7H_8ONI requires I, 51·0%), being thus obtained in colourless plates which turned brown on keeping.

Preparation of the 4-*Halogeno*-m-*cresols*.—On account of the labile nature of the halogen atom in the 4-halogeno-*m*-nitrotoluenes, these cannot be reduced with sodium sulphide. The chloro- and bromo-compounds were reduced with tin and hydrochloric acid, and the iodo-compound with iron and acetic acid as in the preparation of 2-iodoaniline (J., 1925, **127**, 2263). The resulting 4-halogeno-*m*-toluidines, m. p. 30°, 46°, and 37·5°, respectively (Beilstein gives 29—30°, 35°, and 188—189° ?), were converted into the 4-halogeno-*m*-cresols by the method described above in the case of the 4-halogeno-*o*-cresols; the diazotised 4-iodo-*m*-toluidine sulphate, however, was dropped into boiling water instead of boiling dilute sulphuric acid, to avoid splitting off iodine. These 4-halogeno-*m*-cresols have very characteristic odours quite different from those of the 4-halogeno-*o*-cresols. 4-*Chloro*-m-*cresol* has m. p. 45° (Found : Cl, 24·8. C_7H_7OCl requires Cl, 24·9%), and 4-*bromo*-m-*cresol* m. p. 38° (Found : Br, 42·5. C_7H_7OBr requires Br, 42·8%).

In describing the preparation of 2-iodophenol (yield 91%) from 2-iodoaniline (J., 1925, **127**, 2263) we regret that we omitted mention of the very similar method of Holleman and Rinkes (*Rec. trav. chim.*, 1911, **30**, 94), which gives a yield of 80%.

Nitrosation of 4-*Chloro- and* 4-*Bromo*-m-*cresols.*—This was readily effected by the general method (*loc. cit.*). 4-*Chloro*-6-*nitroso*-m-*cresol* crystallised from alcohol, aqueous alcohol, benzene, toluene, and hot dilute hydrochloric acid in needles which varied in shade from yellow to brown and in m. p. (decomp.) from 187° to 191° (Found: Cl, 20·6; N, 8·3%; *M*, cryoscopic in phenol, 156. $C_7H_6O_2NCl$ requires Cl, 20·7; N, 8·2%; *M*, 171·5). 4-*Bromo*-6-*nitroso*-m-*cresol* behaved similarly on crystallisation, the m. p. (decomp.) varying from 187° to 190° (Found: Br, 36·8. $C_7H_6O_2NBr$ requires Br, 37·0%). In both cases the samples crystallised from alcohol had the lowest m. p. and the deepest colour.

Nitrosation of 4-*Iodo*-m-*cresol.*—The general method having proved useless, tarry matter only being formed (compare the nitrosation of 2-iodophenol; *loc. cit.*, p. 2263), the alternative method described in the same place was employed (4-iodo-*m*-cresol, 4 g.; water, 2000 c.c.; sodium nitrite, 10 g.; glacial acetic acid, 5 c.c.; water, 50 c.c.; time of keeping, 16 hours; ethereal extract shaken with aqueous sodium carbonate). The 4-*iodo*-6-*nitroso*-m-*cresol* produced on acidification was obtained, after several recrystallisations from alcohol, in brownish-yellow plates), m. p. 170° (decomp.) (Found: I, 47·9. $C_7H_6O_2NI$ requires I, 48·3%).

The 6-nitroso-compounds give characteristic colours in the Liebermann nitroso-reaction very similar to those of the 5-nitroso-isomerides.

Reduction of 4-*Halogeno*-6-*nitroso*-m-*cresols to* 4-*Halogeno*-6-*amino*-m-*cresols.*—Reduction was effected as in the preparation of 4-halogeno-5-amino-*o*-cresols. The products crystallised from alcohol in faintly brownish-white plates: 4-Chloro-6-amino-*m*-cresol, m. p 227° (slight decomp.) [Kehrmann, *loc. cit.*, gives m. p. 205° and later 218—220° (*Ber.*, 1916, **49**, 1213)]; 4-bromo-6-amino-*m*-cresol, m. p. 222° (slight decomp.) (Kehrmann, *loc. cit.*, gives m. p. 205—208°; Gattermann, *loc. cit.*, gives 215°); 4-*iodo*-6-*amino*-m-*cresol*, prepared from the quinoneoxime, has m. p. 208° (slight decomp.) (Found: I, 50·2. C_7H_8ONI requires I, 51·0%).

Preparation of the 4-*Halogeno*-2 : 5-*toluquinones.*—The 4-halogeno-5-amino-*o*-cresol or 4-halogeno-6-amino-*m*-cresol (5 g.) was dissolved in dilute sulphuric acid (1 : 3), and manganese dioxide (3—4 g.) added. On steam distillation the 4-halogeno-2 : 5-toluquinone was obtained as a yellow solid (yield about 4 g.). Ferric chloride also can be used for the oxidation.

4-Chloro-2 : 5-toluquinone crystallised from alcohol in long, yellow needles, m. p. 104—105° (Vorländer and Schrodter, *Ber.*, 1901, **34**, 165, give m. p. 102°; Schniter, *Ber.*, 1887, **20**, 2286, gives m. p. 105°), 4-bromo-2 : 5-toluquinone in fine, yellow needles, m. p.

105° (Schniter, *loc. cit.*, gives m. p. 105°; Gattermann, *Ber.*, 1894, **27**, 1931, gives m. p. 106°), and 4-*iodo*-2 : 5-*toluquinone* from dilute alcohol in stout needles, m. p. 92°, having the colour of potassium dichromate (Found : I, 51·0. $C_7H_5O_2I$ requires I, 51·2%).

Preparation of the 4-*Halogenotoluquinone*-5-*monoximes*.—Kehrmann and Tichvinsky's procedure (*loc. cit.*) was followed where data were available, but complete details are now given because of the issue raised. The 4-halogeno-2 : 5-toluquinone (1/50 g.-mol.) was dissolved in warm alcohol (80 c.c.), and hydroxylamine hydrochloride (1·4 g.) added gradually with vigorous shaking. The yellow solution darkened to orange and after 18 hours the separated oxime was filtered off.

4-*Chlorotoluquinone*-5-*oxime*. The crude product, yellowish-brown needles, m. p. 183° (decomp.), on crystallisation from toluene gave yellow, feathery needles which, alone or mixed with the corresponding nitroso-compound, melted at 190°. This product corresponds to Kehrmann's sparingly soluble isomeride of m. p. 170°. The alcoholic filtrate, on dilution with water as in Kehrmann's procedure, gave a precipitate which crystallised from alcohol in yellowish-brown needles, from benzene and toluene in yellow, feathery needles, and from hot dilute hydrochloric acid in small, yellow needles, m. p. (decomp.) 187°, 191°, 189°, and 191°, respectively. No trace of Kehrmann's product of m. p. 165° was obtained, and the yield of oxime was quantitative (Found : Cl, 20·6. $C_7H_6O_2NCl$ requires Cl, 20·7%).

4-*Bromotoluquinone*-5-*oxime*. The crude product, m. p. 185°, on crystallisation from benzene or toluene, gave small, yellowish-brown, feathery needles, m. p. 190°. The material obtained by diluting the alcoholic filtrate with water also melted at 190° after recrystallisation. No isomerism was detected (Found : Br, 37·1. $C_7H_6O_2NBr$ requires Br, 37·0%).

4-*Iodotoluquinone*-5-*oxime* crystallises from dilute alcohol in shimmering, golden plates, m. p. 181° (decomp.) (Found : I, 48·1; N, 5·5; *M*, cryoscopic in phenol, 256. $C_7H_6O_2NI$ requires I, 48·3; N, 5·3%; *M*, 263).

The authors thank Messrs. J. W. Leitch & Co. for gifts of chemicals used in this investigation.

THE TECHNICAL COLLEGE,
HUDDERSFIELD.

[*Received, March 31st*, 1926.]

CCLXXIV.—*Orientation Effects in the Diphenyl Series. Part III. The Mononitro-4 : 4′-dihalogenodiphenyls and Some Allied Compounds.*

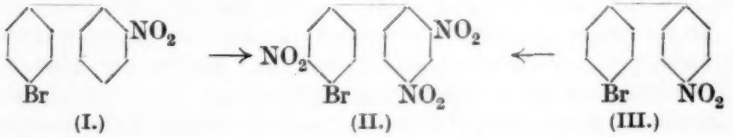
By Raymond James Wood Le Fèvre and Eustace Ebenezer Turner.

In Part I of this series (this vol., p. 476) it was concluded that the product of mononitration of 4 : 4′-dibromodiphenyl (Lellmann, *Ber.*, 1882, **15**, 2837) was the 2-nitro-derivative, and further investigation of this compound therefore seemed desirable. We have attempted to prepare it by other methods, as follows: (1) from 2-nitrobenzidine, using the perbromide method of Griess-Saunders, (2) from 2-nitrodiphenyl by direct bromination, and (3) from 4-bromo-4′-aminodiphenyl (see Experimental).

2-Nitrobenzidine, under the conditions of a perbromide displacement, gave, not 4 : 4′-dibromo-2-nitrodiphenyl, but a substance which we regard as 3′ : 4 : 4′-*tribromo-2-nitrodiphenyl*.

2-Nitrodiphenyl, when brominated in the cold in presence of ferric chloride, readily gave 4-bromo-2′-nitrodiphenyl (I), obtained by Schultz, Schmidt, and Strasser (*Annalen*, 1881, **207**, 311) from 2′-nitro-4-aminodiphenyl. The bromonitro-compound could not, however, be further brominated to give Lellmann's compound (above).

4-Bromo-2′-nitrodiphenyl nitrated readily to give 4-*bromo*-2′ : 3 : 4′-*trinitrodiphenyl* (II), whose constitution is established (*a*) by its conversion by piperidine into 2′ : 3 : 4′-*trinitro*-4-*piperidinodiphenyl*, and (*b*) by its formation also by the nitration of 4-bromo-4′-nitrodiphenyl (III).



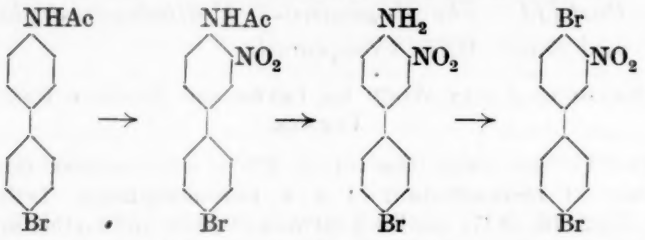
(I.) (II.) (III.)

The restricted nitration of 4 : 4′-dibromodiphenyl was accordingly studied afresh, and a satisfactory method has been found (see Experimental) for the preparation of the 2-nitro-derivative, avoiding the extravagant conditions described by Lellmann.

By the restricted nitration of 4 : 4′-dichlorodiphenyl under similar conditions, 4 : 4′-*dichloro*-2-*nitrodiphenyl* was obtained. Its constitution follows from its inertness towards piperidine.

It was now necessary to prepare 4 : 4′-*dibromo*-3-*nitrodiphenyl* in order to discover whether this, like its isomeride, would be quantita-

tively nitrated to give the 2 : 3′-dinitro-compound. The following scheme denotes the reactions which gave the desired result :



4-Nitrodiphenyl brominated readily in glacial acetic acid at 100° to give 4-bromo-4′-nitrodiphenyl (III). The nitration of 4-bromo-4′-acetylaminodiphenyl gave the 3′-nitro-compound, whose constitution was proved by its conversion into a 4 : 4′-dibromonitrodiphenyl, m. p. 101—102°, which reacted with piperidine, depressed the m. p. of 4 : 4′-dibromo-2-nitrodiphenyl, and is evidently the desired 4 : 4′-*dibromo-3-nitrodiphenyl.* The identity of Lellmann's compound is thus, incidentally, set beyond all doubt.

Nitration of 4 : 4′-dibromo-3-nitrodiphenyl gave 4 : 4′-dibromo-2 : 3′-dinitrodiphenyl, together with a second substance (probably the 3 : 3′-dinitro-compound) from which it could not be separated. When the crude nitration product was heated with piperidine, there resulted a mixture of piperidino-derivatives, from which pure 4-bromo-4′-piperidino-2 : 3′-dinitrodiphenyl (Dennett and Turner, Part I, *loc. cit.*) was isolated. Thus, whilst 4 : 4′-dibromo-2 : 3′-dinitrodiphenyl is formed *quantitatively* by the nitration of the 2-nitro-derivative, it is accompanied by an isomeride when prepared by the nitration of the 3-nitro-compound. Further, 4 : 4′-dichloro-2-nitrodiphenyl is the first substance formed during the conversion of 4 : 4′-dichlorodiphenyl into its 2 : 3′-dinitro-derivative.

In our earlier attempts to prepare 4 : 4′-dibromo-3-nitrodiphenyl, it was hoped to make use of 3-nitrobenzidine. Koller (*Ber.*, 1904, **37**, 2880) described the preparation of this substance, m. p. 190°, by the nitration of monophthalylbenzidine,* and hydrolysis of the resulting mononitro-compound. We carefully followed Koller's directions

* Other allied experiments have shown that monophthalylbenzidine does not possess the structure assumed by Koller (*loc. cit.*) and by Kaufler (*Annalen*, 1907, **351**, 151), but contains instead a free amino-radical, and therefore a phthalylamino-group. The formation of 2-nitrobenzidine mentioned above is not surprising, since the "amino-sulphate" group has a pronounced meta-orienting influence, and the phthalylamino-group is known not to exhibit any appreciable ortho-para orienting effect when other substituents are present (Cain and Micklethwait, J., 1914, **105**, 1442; Brady, Quick, and Welling, J., 1925, **127**, 2264). An investigation of the structures of other "Kaufler compounds" is now in progress.

for nitration on six different occasions. Each time, the bulk of the product was 2-nitrobenzidine, and no isomeric nitrobenzidine having the properties mentioned by Koller was isolated.

Since the nitration of diacetylbenzidine in excess of nitric acid gives 3 : 3′-dinitrodiacetylbenzidine (Strakosch, *Ber.*, 1872, **5**, 236; Cain, Coulthard, and Micklethwait, J., 1912, **101**, 2298; Le Fèvre and Turner, this vol., p. 1759), it might seem that the mononitration of diacetylbenzidine would yield 3-nitrodiacetylbenzidine. This has been investigated, but, owing to the highly insoluble nature of diacetylbenzidine, we were compelled to use concentrated sulphuric acid as a solvent. Only impure 2-nitrobenzidine was isolated. A similar meta-directing influence on the part of an acetylamino-group under these conditions was noted by Koller (*Ber.*, 1903, **36**, 410), the nitration of *p*-acetylaminophenyloxamic acid in concentrated sulphuric acid giving 4-acetylamino-2-nitrophenyloxamic acid.

In Parts I and II of this series, reference was made to the action of reagents other than piperidine on dihalogenodinitrodiphenyls. Some *phenoxy-*, *amino-*, *anilino-*, *methylanilino-*, and *piperazino-*derivatives of 2 : 3′- and 3 : 3′-dinitrohalogenodiphenyls are now described.

Experimental.

Perbromide Displacement on 2-Nitrobenzidine.—The nitrobenzidine was diazotised in sulphuric acid, and the solution treated with bromine dissolved in hydrobromic acid. The perbromide separated as an oil, which slowly became an orange solid. This was washed, pressed, and boiled with glacial acetic acid until bromine evolution ceased. The resulting solution, on cooling, became a magma of crystals, which were washed with spirit and once recrystallised from glacial acetic acid, 3 : 4 : 4′-*tribromo-2′-nitrodiphenyl* (?) being obtained in needles, m. p. 195—196° (Found : N, 3·6; Br, 55·2; *M*, in camphor by Rast's method, 450. $C_{12}H_6O_2NBr_3$ requires N, 3·2; Br, 55·0%; *M*, 436). The molecular weight was determined in order to distinguish the compound from the other possible product, a hexabromodinitrobenzerythrene (requiring N, 3·2; Br, 55·1%; *M*, 870).

Bromination of 2-Nitrodiphenyl.—A mixture of 22·5 g. of the nitro-compound, 8 c.c. of bromine, 1 g. of ferric chloride, and 25 c.c. of water was well stirred, and then left over-night. After removal of the excess of bromine by means of sodium carbonate, followed by crystallisation from alcohol, 4-bromo-2′-nitrodiphenyl was obtained in good yield. Attempts to brominate the product further, by means of bromine and ferric chloride, either in the cold or at high temperatures under pressure, were unsuccessful.

Nitration of 4-*Bromo*-2′-*nitrodiphenyl*.—This substance was dissolved in nitric acid (*d* 1·5; 7 parts by wt.) at the ordinary temperature. After 2 minutes, the solution was rapidly diluted, the product collected, and crystallised from glacial acetic acid. 4-*Bromo*-2′ : 3 : 4′-*trinitrodiphenyl* was thus obtained as cream-coloured needles, m. p. 176—177°, sparingly soluble in alcohol (Found: Br, 21·8. $C_{12}H_6O_6N_3Br$ requires Br, 21·7%).

When the last-named compound was warmed for 1 minute with excess of piperidine, it was converted into 2′ : 3 : 4′-*trinitro*-4-*piperidinodiphenyl*, which crystallised from glacial acetic acid in scarlet plates, m. p. 144—145° (Found: N, 15·3. $C_{17}H_{16}O_6N_4$ requires N, 15·0%).

Nitration of 4-*Bromo*-4′-*nitrodiphenyl*.—This substance was nitrated by the method used for the 2′-nitro-compound, and gave 4-bromo-2′ : 3 : 4′-trinitrodiphenyl, identical with the specimen obtained from 4-bromo-2′-nitrodiphenyl. Identity was further confirmed by means of the piperidino-derivatives.

4-*Bromo*-2′-*nitro*-4′-*aminodiphenyl*.—When 4-bromo-4′-aminodiphenyl (see below) was nitrated in excess of concentrated sulphuric acid a product was obtained which could not be crystallised. It was therefore converted into the acetyl derivative, which melted at about 151°. Hydrolysis gave the amino-compound as a yellow solid, m. p. about 180°. This could not be purified further, and a perbromide displacement gave a gummy product from which no chemical individual was isolated.

Restricted Nitration of 4 : 4′-*Dibromodiphenyl*.—To a solution of the dibromo-compound (10 g.) in a mixture of 100 c.c. of acetic acid and 100 c.c. of acetic anhydride at 85—90°, 5 g. of potassium nitrate in 30 c.c. of concentrated sulphuric acid were added slowly. After being heated for a further 20 minutes, the solution was cooled, the dibromodiphenyl that separated (1·7 g.) was removed, and the residue diluted with water. The resulting precipitate melted at 110—115° after drying, and at 124° after four crystallisations from alcohol. One further crystallisation from light petroleum (b. p. 80—100°) and then two crystallisations from alcohol failed to raise the m. p.* (Particular care was taken in purifying this substance because of its indefinite crystalline appearance.)

Restricted Nitration of 4 : 4′-*Dichlorodiphenyl*.—A well-stirred

* Nitration by this method gave 2 g. (22% yield) of the pure material. The process described by Lellmann affords a product which is very difficult to purify. About 500 g. of fuming nitric acid are required for the preparation of a gram or so of the pure nitro-compound. As Lellmann says: "Da das Dibromdiphenyl in Eisessig schwer löslich ist, so ist die Ausbeute an Mononitrodibromdiphenyl eine geringe." We are unable to account for the m. p. (127°) recorded by Lellmann.

solution of 5·6 g. of dichlorodiphenyl in 100 c.c. of glacial acetic acid and 10 c.c. of acetic anhydride was slowly treated at 90° with a solution of 3·5 g. of potassium nitrate in a little sulphuric acid, and thereafter the temperature was kept at 100° for ½ hour. On cooling, 2 g. of unchanged dichlorodiphenyl separated. The solution was diluted, and the resulting bright yellow solid (3 g.) dissolved in a little hot alcohol. On cooling, the yellow nitro-compound and the white dichloro-compound separated together, and this occurred after three further crystallisations. Three subsequent crystallisations from alcohol, in which the boiling solution was allowed to cool partially, followed by two crystallisations from carbon tetrachloride, gave 4 : 4′-*dichloro*-2-*nitrodiphenyl* as yellow needles, m. p. 102° (Found : Cl, 26·3. $C_{12}H_7O_2NCl_2$ requires Cl, 26·5%). The nitro-compound was unaffected by piperidine, and was not accompanied, in its formation, by any isomeride.

4-*Bromo*-4′-*nitrodiphenyl*.—A mixture of 4-nitrodiphenyl (45 g.), glacial acetic acid (90 c.c.), and bromine (22·3 c.c.) was heated at 100° for 3·5 hours (longer heating diminished the yield), cooled, and filtered. The resulting solid crystallised from about 300 c.c. of glacial acetic acid in slightly brown needles, m. p. 170—172° (yield, 80%). The product was sufficiently pure for use in the next stage (compare Schultz, *Annalen*, 1874, **174**, 218).

4-*Bromo*-4′-*amino- and* 4-*Bromo*-4′-*acetylamino-diphenyl*.—A boiling solution of 50 g. of the bromonitro-compound in 400 c.c. of alcohol was treated slowly with a solution of 180 g. of stannous chloride crystals in 200 c.c. of concentrated hydrochloric acid. Heating was then continued for an hour (bath at 100°). On cooling, plates separated. These were stirred with excess of alkali and the resulting amino-compound was collected and crystallised from alcohol. Thus obtained, it melted at 142—143° (Gelmo, *Ber.*, 1906, **39**, 4175, gives 145° corr.). 30 G. were boiled for 2 hours with a mixture of 75 c.c. of acetic acid and 40 c.c. of acetic anhydride; after the usual procedure, 33 g. of 4-bromo-4′-acetylaminodiphenyl were obtained (see Gelmo, *loc. cit.*).

4-*Bromo*-3′-*nitro*-4′-*acetylaminodiphenyl*.—A solution of the preceding acetyl compound (32 g.) in a mixture of 400 c.c. of glacial acetic acid, 160 c.c. of acetic anhydride, and 160 c.c. of concentrated sulphuric acid was kept at 0° and treated with 12 g. of potassium nitrate. After 12 hours the solution was warmed to 50° for 20 minutes, cooled and poured on to ice. The light yellow powder, so obtained, after two crystallisations from acetic acid, gave plates, m. p. 199—200° (Found : Br, 24·2. $C_{14}H_{11}O_3N_2Br$ requires Br, 23·9%).

4-*Bromo*-3′-*nitro*-4′-*aminodiphenyl*.—The preceding compound

was heated for 30 minutes at 140° with a mixture of equal volumes of concentrated sulphuric acid and water. The solution was cooled, basified with ammonia and the precipitate collected. It did not crystallise well from any of the common solvents, but was obtained pure by solution in *o*-dichlorobenzene and partial precipitation with light petroleum, forming brown needles, m. p. 174—175° (Found: Br, 27·1. $C_{12}H_9O_2N_2Br$ requires Br, 26·9%).

4 : 4′-*Dibromo*-3-*nitrodiphenyl*.—The preceding amine was dissolved in concentrated sulphuric acid (10 parts), and ice added until a precipitate just began to form. Solid sodium nitrite (1 mol.) and, at intervals, ice were added. The filtered solution, when treated with a mixture of bromine and hydrobromic acid, gave the *perbromide* as a reddish-orange, crystalline precipitate. This was boiled with acetic acid, and the resulting solution diluted; the dibromo-compound which separated crystallised from alcohol in cream-coloured plates, m. p. 101—102° (Found: Br, 44·9; *M*, in camphor by Rast's method, 352. $C_{12}H_7O_2NBr_2$ requires Br, 44·8%; *M*, 357. $C_{24}H_{12}O_4N_2Br_4$, the corresponding tetrabromodinitrobenzerythrene, requires Br, 44·9%; *M*, 712).

4-*Bromo*-3′-*nitro*-4′-*piperidinodiphenyl*, readily obtained by heating the dibromo-compound with piperidine, separated from alcohol in bright yellow plates, m. p. 85° (Found: Br, 26·7. $C_{17}H_{17}O_2N_2Br$ requires Br, 26·9%).

Nitration of 4 : 4′-*Dibromo*-3-*nitrodiphenyl*.—This substance was warmed with excess of nitric acid (*d* 1·5) for 1 minute, the solution rapidly diluted, and the yellow precipitate dried. It had m. p. 110—125° and could not be purified by crystallisation. Extraction with benzene, however, left a solid, m. p. 190—200° alone or 210—215° when mixed with 4 : 4′-dibromo-3 : 3′-dinitrodiphenyl, with which it is probably identical. The latter substance would appear to be the only possible dibromodinitrodiphenyl (melting above 200°) that could be formed in the above circumstances.

The crude nitration mixture was boiled with excess of piperidine. The gummy product became solid after repeated washing with hot water and was then recrystallised four times from alcohol. The yellow crystals so obtained melted at 135°. A mixture with an authentic specimen of 4-bromo-2 : 3′-dinitro-4′-piperidinodiphenyl melted at 135—136°.

Nitration of Monophthalylbenzidine.—Monophthalylbenzidine was prepared and nitrated exactly as described by Koller (*loc. cit.*). The nitration product was hydrolysed either with cold ammonia as recommended by Koller or by heating with 60% sulphuric acid for 20 minutes at 140°. In the former case a mixture was produced the separation of which was difficult, but in the latter case, when the

acid solution was cooled, impure 2-nitrobenzidine sulphate crystallised, a partial separation being thus effected. It was found best, however, to liberate the mixture of free bases, dissolve them in excess of hydrochloric acid, filter the solution from the yellowish-brown sludge, and precipitate the bases fractionally with ammonia. Repeated applications of this process led to separation into two main fractions, m. p. about 127° and m. p. about 200°, respectively. The former, after repeated crystallisation, gave pure 2-nitrobenzidine, whilst the latter could not be purified, but was probably impure 2 : 3′-dinitrobenzidine, formed by the nitration of 2-nitrophthalylbenzidine.

Nitration of Diacetylbenzidine.—A solution of 36 g. of diacetylbenzidine in 120 c.c. of concentrated sulphuric acid was cooled to −3° to −5° and slowly nitrated with 12 g. of potassium nitrate dissolved in 30 c.c. of concentrated sulphuric acid. After being stirred for 10 minutes, the mixture was diluted with water, and the resulting yellow precipitate washed with boiling alcohol, and hydrolysed at once with excess of 60% sulphuric acid at 140° for 20 minutes. After cooling, dilution and basification, a reddish-brown product was obtained from which only 2-nitrobenzidine could be isolated. Variation of the conditions of nitration produced no essential difference in the result.

Displacement Products from 4 : 4′-*Dichloro- and* 4 : 4′-*Dibromo-*2 : 3′-*dinitrodiphenyls.*—The anilino-, methylanilino-, and piperazino-derivatives described below were formed by gently boiling a solution of the halogen compound concerned with about 10 parts of the appropriate base for 5 minutes. On cooling, the base hydrochloride or hydrobromide crystallised. The magma was stirred with dilute hydrochloric acid to remove excess of amine, the product washed with water, and recrystallised from a suitable solvent.

4-*Bromo*-2 : 3′-*dinitro*-4′-*anilinodiphenyl* crystallises from glacial acetic acid in spherical aggregates of orange microscopic needles, m. p. 151° (Found : Br, 19·1. $C_{18}H_{12}O_4N_3Br$ requires Br, 19·3%).

4-*Chloro*-2 : 3′-*dinitro*-4′-*anilinodiphenyl* separates from dilute acetic acid in orange-yellow, microscopic needles, m. p. 129—130° (Found : Cl, 9·5. $C_{18}H_{12}O_4N_3Cl$ requires Cl, 9·6%).

4-*Bromo*-2 : 3′-*dinitro*-4′-*methylanilinodiphenyl* separates from alcohol in yellow plates, m. p. 142—143° (Found : Br, 9·4. $C_{19}H_{14}O_4N_3Br$ requires Br, 9·8%).

4-*Chloro*-2 : 3′-*dinitro*-4′-*methylanilinodiphenyl* crystallises from alcohol in golden-yellow, rectangular platelets, m. p. 134° (Found : Cl, 9·2. $C_{19}H_{14}O_4N_3Cl$ requires Cl, 9·3%).

4-*Bromo*-2 : 3′-*dinitro*-4′-*phenoxydiphenyl.*—To the hot solution

produced by mixing 3 g. of potassium hydroxide, 1 c.c. of water, and 20 g. of phenol, 2 g. of 4 : 4′-dibromo-2 : 3′-dinitrodiphenyl were added, and the whole was boiled for a few minutes. After cooling and treatment with water, a yellow powder was obtained which crystallised from glacial acetic acid in pale yellowish-green, hairy needles, m. p. 124—125° (Found : Br, 19·1. $C_{18}H_{11}O_5N_2Br$ requires Br, 19·3%).

4-*Chloro*-2 : 3′-*dinitro*-4′-*phenoxydiphenyl*, prepared like the bromo-compound, crystallises from glacial acetic acid in pale greenish-yellow, hairy needles, m. p. 113° (Found : Cl, 9·6. $C_{18}H_{11}O_5N_2Cl$ requires Cl, 9·6%).

4-*Bromo*-2 : 3′-*dinitro*-4′-*piperazinodiphenyl* was obtained by heating 3 g. of dibromodinitrodiphenyl with 3·5 g. of piperazine for 2 minutes. The product, obtained on dilution with water, crystallised from *o*-dichlorobenzene in yellow, microscopic plates, m. p. above 250° (Found : Br, 19·1. $C_{16}H_{15}O_4N_4Br$ requires Br, 19·6%).

4-*Chloro*-2 : 3′-*dinitro*-4′-*piperazinodiphenyl*, prepared similarly, separates from alcohol as a yellowish-orange, amorphous powder, which blackens above 200° and does not melt at 250° (Found : Cl, 9·2. $C_{16}H_{15}O_4N_4Cl$ requires Cl, 9·8%).

Similarly, when the dihalogeno-2 : 3′-dinitro-compounds were heated with aqueous-alcoholic ammonia at 140—160° for 8 hours under pressure, the following compounds were obtained : 4-*Chloro*-2 : 3′-*dinitro*-4′-*aminodiphenyl*, long, orange needles, from alcohol, m. p. 218—219° (Found : Cl, 12·0. $C_{12}H_8O_4N_3Cl$ requires 12·1%), and 4-*bromo*-2 : 3′-*dinitro*-4′-*aminodiphenyl*, yellow needles, m. p. 219° (Found : Br, 23·8. $C_2H_8O_4N_3Br$ requires 23·7%).

Displacement Products from 4 : 4′-*Dibromo*-3 : 3′-*dinitrodiphenyl*.—Bases reacted with this substance to give products which were much less soluble than the corresponding substances obtained from the 2 : 3′-compound.

3 : 3′-*Dinitro*-4 : 4′-*dianilinodiphenyl* separates from pyridine in reddish-brown, microscopic needles, m. p. 242° (Found : N, 13·8. $C_{24}H_{18}O_4N_4$ requires N, 13·1%).

3 : 3′-*Dinitro*-4 : 4′-*dimethylanilinodiphenyl* is sparingly soluble in acetic acid, and crystallises from pyridine in light brown, rectangular plates, m. p. 250° (Found : N, 12·8. $C_{26}H_{22}O_4N_4$ requires N, 12·3%). (All three methylanilino-derivatives have the same crystalline appearance under the microscope.)

3 : 3′-*Dinitro*-4 : 4′-*diphenoxydiphenyl*.—In the preparation of this substance a reddish-brown tar containing diphenols results if water is present. Potassium hydroxide (5 g.) was dissolved in 30 c.c. of molten phenol, and 2 g. of the dibromodinitro-compound were added. The mixture was boiled for 5 minutes, cooled somewhat,

and diluted first with alcohol, and then with water. The greenish-yellow precipitate, after being twice crystallised from glacial acetic acid, became a yellow, microcrystalline powder, m. p. 139—140° (Found : N, 6·8. $C_{24}H_{16}O_6N_2$ requires N, 6·5%).

The authors desire to thank Mr. F. Bell, B.Sc., for a gift of 2-nitrodiphenyl, and the Research Fund Committee of the Chemical Society for allocating a grant in aid of the present work, which is being continued.

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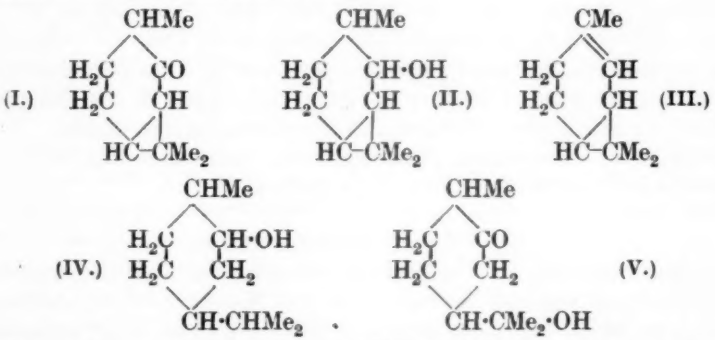
CCLXXV.—*The Catalytic Hydrogenation of Carone.*

By SUBRAMANIA NARAYANA IYER and JOHN LIONEL SIMONSEN.

DURING the course of his researches on the terpenes Baeyer (*Ber.*, 1894, **27**, 1913) prepared the dicyclic ketone carone (I), and until the separation of the two hydrocarbons Δ^3- and Δ^4-carene from the essential oils obtained from *P. longifolia* and *A. Jwarancusa* (J., 1920, **117**, 570; 1922, **122**, 2292) this was the only known substance of the terpene group possessing this dicyclic structure. In view of the probable wide occurrence of these dicyclic hydrocarbons in nature it appeared to us of interest to attempt the synthesis of Δ^4-carene (III). The simplest method available would be the elimination of water from the secondary alcohol (II) which should result from the reduction of carone.



It was shown by Baeyer (*Ber.*, 1895, **28**, 1601) that when carone in moist ethereal solution was reduced with sodium *p*-menthan-2-ol (IV) was produced, whilst treatment of the cyclic ketone with sodium and amyl formate with subsequent decomposition of the hydroxymethylene derivative yielded the corresponding mono-

cyclic ketone. A further indication of the marked instability of the dicyclic system was the fact, also observed by Baeyer (*Ber.*, 1896, **29**, 16), that in the presence of dilute sulphuric acid carone was converted into *p*-menthan-8-ol-2-one (V). It was obvious from these experiments that carone behaved more like an αβ-unsaturated ketone than a dicyclic ketone, but it seemed to us that it might prove possible to hydrogenate it catalytically to the secondary alcohol (II).

Unfortunately, this was found not to be the case. Under the conditions described in the experimental section, after the absorption of 1 mol. of hydrogen, the product consisted mainly of *p*-menthan-2-one mixed with unchanged carone and other substances; on complete reduction (2 mols. of hydrogen), *p*-menthane (in small quantity), *p*-menthan-2-ol (IV), and *l*-*p*-menthane-2 : 8-diol were obtained.

The *p*-menthan-2-ol (IV) obtained was optically inactive and differed in one particular only from the racemic alcohol described by Wallach (*Annalen*, 1893, **277**, 132)—the phenylurethane melted at 107° and not at 75—76°. This discrepancy is in all probability due to the fact that the two alcohols are stereoisomeric, since four racemic forms are possible.

The formation of *l*-*p*-menthane-2 : 8-diol during the hydrogenation is of some interest and it would appear to have been formed by the hydration of the *cyclo*propane ring by the very dilute hydrochloric acid present in the reaction mixture, the hydroxy-ketone subsequently undergoing reduction.

It is somewhat remarkable that no evidence was obtained of the presence of *m*-cymene derivatives, nor does there appear to be any tendency for *cyclo*heptane derivatives to be formed. Although these experiments have not proceeded in the desired direction, they are not without interest since they show quite clearly the great tendency of carone to behave like an αβ-unsaturated ketone. It is proposed to investigate other reactions with carone in order to determine how far this property is general.

Experimental.

The carone required for these experiments was most conveniently prepared in quantity by the method of Kondakov and Gorbanov (*J. pr. Chem.*, 1897, **56**, 256). It had b. p. 150—153°/100 mm., $d_{30}^{30°}$ 0·9468, $n_D^{30°}$ 1·4739, and $[\alpha]_D^{30°}$ — 250°.

The most satisfactory method of hydrogenation is the following: The ketone (10 g.) was dissolved in acetic acid (20 c.c.), platinic chloride solution (Pt, 10%; 5 c.c.) and gum arabic solution (gum arabic, 2%; 20 c.c.) were added, and the bottle containing the

mixture was evacuated and filled with hydrogen. A solution of colloidal palladium (1 c.c.) was added, the apparatus again evacuated, and filled with hydrogen at a pressure of 2 atmospheres. The mixture was mechanically shaken; hydrogen was rapidly absorbed during 2—2½ hours until approximately 2 litres (2 mols.) had been taken up. The mixtures from a number of such experiments were combined and, after separation of the platinum, the oil was taken up with ether, the ether washed with sodium carbonate solution until free from acetic acid, dried, and evaporated. The residual oil partly crystallised on keeping. The solid (A) was collected, and the filtrate distilled under diminished pressure (100 mm.); three main fractions were then obtained, (i) 105—115°, (ii) 135—140°, (iii) 140—180°. The small residue crystallised and was added to (A).

p-*Menthane*.—Fraction (i) was repeatedly distilled over sodium; it then had b. p. 168—169°/685 mm., $d_{30^\circ}^{30^\circ}$ 0·7984, $n_D^{30^\circ}$ 1·435, was optically inactive, had a smell resembling that of light petroleum and was not attacked by warm alkaline permanganate (Found: C, 86·0; H, 13·9. Calc.: C, 85·7; H, 14·3%). The small quantity available did not permit the preparation of crystalline derivatives, but there would appear to be no doubt that the substance is *p*-menthane.

p-*Menthan*-2-*ol*.—The higher fractions were kept for some days in the ice-box and after removal of the solid deposited (this was added to A), the filtrate was heated with alcoholic potassium hydroxide to hydrolyse any acetyl derivative present. The cyclic alcohol was distilled in steam and then under diminished pressure; b. p. 143—144°/100 mm., $d_{30^\circ}^{30^\circ}$ 0·9004, $n_D^{30^\circ}$ 1·457. It was optically inactive (Found: C, 76·9; H, 12·6. Calc.: C, 76·9; H, 12·8%). The *phenylurethane* crystallised from light petroleum in needles, m. p. 107—108° (Found: N, 5·4. Calc.: N, 5·1%).

The alcohol (10 g.) was oxidised in acetic acid solution with a slight excess of chromic acid; the *p*-menthan-2-one obtained, b. p. 146—148°/100 mm., was identified by means of the oxime, m. p. 105°, and the semicarbazone, m. p. 194—195°, which were compared with authentic specimens.

On oxidation with alkaline permanganate the ketone gave β-*iso*propyladipic acid, which was purified through the calcium salt and recrystallised from water, from which it tended to separate as an oil. The acid was very difficult to purify and melted at 78—80° (Found for the silver salt: Ag, 54·1. Calc.: Ag, 53·7%). Previous workers (Wallach and Koehler, *Annalen*, 1905, **339**, 113; Wallach, *ibid.*, 1906, **343**, 33; 1917, **414**, 287) also have found the acid difficult to crystallise.

1-p-*Menthane*-2 : 8-*diol*.—The solid (A) crystallised from ethyl acetate in large, glistening prisms, m. p. 155—156°, $[\alpha]_D^{20°}$ − 40° in chloroform (Found: C, 69·7; H, 11·4. Calc.: C, 69·8; H, 11·6%). It was identified with *l*-*p*-menthane-2 : 8-diol (Wallach, *Annalen*, 1917, **414**, 195) (1) by treating it with an acetic acid solution of hydrogen bromide for some days; the solid obtained on addition of water crystallised from methyl alcohol in plates, m. p. 57—58°, and was shown by direct comparison to be terpinene dihydrobromide, (2) by oxidising it in acetic acid with a slight excess of chromic acid; *p*-menthan-8-ol-2-one was obtained, and identified by means of the semicarbazone, m. p. 149° (Found: N, 18·6. Calc.: N, 18·5%).

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[*Received, May 11th*, 1926.]

CCLXXVI.—*The Alcohols of the Hydroaromatic and Terpene Series. Part V. The Geometrical and Optical Isomerism of the Methylcyclohexanols.*

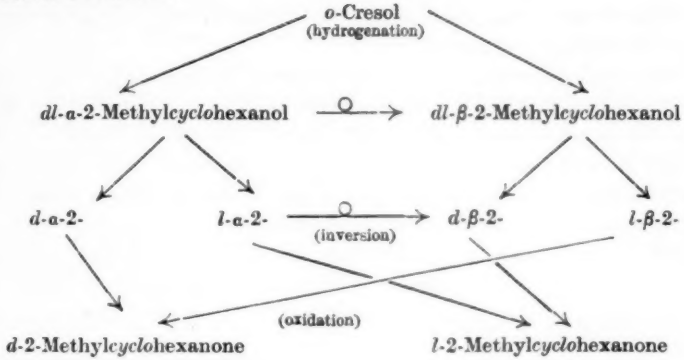
By GEORGE ALECK CROCKER GOUGH, HAROLD HUNTER, and JOSEPH KENYON.

MODERN chemical theory predicts that both hexahydro-*o*-cresol and hexahydro-*m*-cresol should exist in two geometrically isomeric forms, each capable of resolution into optical antipodes, and, further, that hexahydro-*p*-cresol should exist in two geometrically isomeric forms incapable of such resolution. Although many indications occur in chemical literature of the partial separation of these substances, no conclusive evidence of their isolation in a pure state exists. These substances have now been prepared and evidence of their chemical purity will be given.

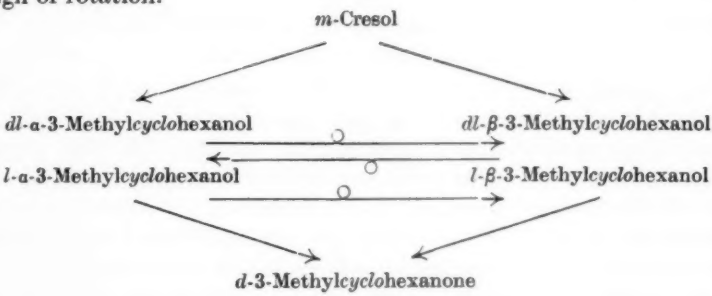
The two isomeric methyl*cyclo*hexanols derived from each cresol are characterised by widely differing viscosities and the convention has been adopted of naming the more viscous isomeride the α- and the less viscous the β-. It will be pointed out, nevertheless, that in all probability the α-isomerides are the *trans*-, and the β- the *cis*-methyl*cyclo*hexanols. By means of a viscosity–composition diagram, constructed for mixtures of α- and β-2-methyl*cyclo*hexanols, it has been found possible to study the effect of experimental conditions on the relative proportions of the two isomerides formed by various methods of preparation.

It is possible to effect the complete geometrical interconversion of the α- and β- forms of the methyl*cyclo*hexanols through the medium

of the *p*-toluene-sulphonic esters. Partly in this way and partly by the oxidation of the optically active methyl*cyclo*hexanols to the corresponding ketones, the relative configurations of the isomerides have been deduced. The following diagram represents some of the results obtained :



In the case of the isomerides derived from *m*-cresol somewhat different results were obtained, since the *l*-α- and the *l*-β-3-methyl*cyclo*hexanols yielded the same ketone on oxidation, whereas the *l*-α-2- and the *l*-β-2-methyl*cyclo*hexanols yielded ketones of opposite sign of rotation.



(*a*) *Preparation of the Geometrical Isomerides of Methyl*cyclo*hexanol.*

Numerous investigators have prepared derivatives of the methyl*cyclo*hexanols and have generally assumed that the reduction product of the corresponding cresol or ketone is homogeneous. Three instances, however, are recorded in which samples of methyl*cyclo*hexanol, derived from the same parent compound, have been found to possess different properties : Knoevenagel (*Annalen*, 1897, **297**, 150) synthesised 3-methyl*cyclo*hexanol from acetoacetic ester and formaldehyde ; two variations of the synthesis yielded products with slightly different physical properties. Skita (*Annalen*, 1923,

431, 1) hydrogenated the three cresols under various conditions and obtained from each two different products. Godchot and Bedos (*Compt. rend.*, 1922, **174**, 461; *Bull. Soc. chim.*, 1925, **37**, 1451) showed that the 2-methyl*cyclo*hexanol prepared by the hydrogenation of *o*-cresol (Sabatier and Mailhe, *Compt. rend.*, 1905, **140**, 350) differed from that obtained by the action of magnesium methyl iodide on *cyclo*hexene oxide.

In the work now described, the mixture of isomerides resulting from the hydrogenation of each cresol has been separated by the fractional crystallisation of a solid ester. In the cases of the 2- and the 4-methyl*cyclo*hexanols, two pure products were obtained in each instance by crystallisation of the hydrogen phthalic esters. This method could not be used to separate the isomerides in hydrogenated *m*-cresol, since the mixture of hydrogen phthalic esters crystallised only with extreme slowness. Systematic fractional crystallisation of the *p*-nitrobenzoic esters, however, yielded two pure substances.

The homogeneity of these compounds was tested in all cases by crystallisation from various solvents. The pure esters were separately hydrolysed and the free methyl*cyclo*hexanols, thus obtained, converted into other solid derivatives; these, also, were found to suffer no change on repeated crystallisation.

(*b*) *The Optically Active Forms of the Geometrical Isomerides of* 2- *and of* 3-*Methyl*cyclo*hexanols.*

α- *and* β-2-*Methyl*cyclo*hexanols.*—The optically active forms of both these alcohols were obtained by the systematic fractional crystallisation of alkaloidal salts of their hydrogen phthalic esters. These optical resolutions presented difficulties similar to those encountered in the resolution of *dl*-menthol and of *dl-neo*menthol (Pickard and Littlebury, J., 1912, **101**, 109) and in both cases special methods had to be employed in order to attain optical purity.

α- *and* β-3-*Methyl*cyclo*hexanols.*—*d*-3-Methyl*cyclo*hexanone, obtained by the action of hydrolytic agents on pulegone (Wallach, *Annalen*, 1896, **289**, 337), was reduced and the resulting mixture of 3-methyl*cyclo*hexanols converted into their *p*-nitrobenzoic esters. Crystallisation of this mixture yielded an ester unaltered by further crystallisation, which, on hydrolysis, gave *l*-α-3-methyl*cyclo*hexanol with the same viscosity and density as that obtained from *m*-cresol.

It was not found possible to separate the optically active β-ester from the complex mixture of esters in the mother-liquors, owing possibly to the fact that, since the natural ketone is not optically pure, the mixture of esters contains small amounts of the *dl*-α-,

dl-β-, and *l*-β- as well as the *l*-β-ester which was isolated. *l*-β-3-Methyl*cyclo*hexanol was obtained by the geometrical inversion of the *l*-α-alcohol by the methods described in section (*e*) of this paper.

The optical purity of *l*-α-3- and of *l*-β-3-methyl*cyclo*hexanols, both of which yield the 3-methyl*cyclo*hexanone of the same sign and magnitude of optical rotatory power on oxidation, was confirmed by converting *l*-α-3-methyl*cyclo*hexanol into the hydrogen phthalic ester and fractionally crystallising the strychnine salt of this ester. No alteration of the rotatory power of the ester could be obtained.

α-4-*Methyl*cyclo*hexanol*.—Although this substance possesses a symmetrical structure according to the classical theories, an attempt was made, nevertheless, to obtain it in optically active forms by the crystallisation of the strychnine salt of the hydrogen phthalic ester, but without success.

(*c*) *The Physical Properties of the Geometrical Isomerides.*

It was found that the members of the complete series of six geometrical isomerides possessed widely differing viscosities and since the importance of viscosity as a means of studying geometrical isomerism has been emphasised by Thole (J., 1912, **101**, 552), it is of interest to develop the matter theoretically.

Discussing the relation between viscosity and geometrical isomerism in the light of the work of Beck on the viscosity of fused oximes (*Z. physikal. Chem.*, 1904, **48**, 674) and of his own on the viscosity of geometrically isomeric acids and their esters, Thole suggests that two sets of factors are operative :

(*A*) When the groups responsible for geometrical isomerism possess small residual affinity, the *cis*-compound will have the greater viscosity, since the proximity of these groups tends spatially to potential ring formation—a condition which is well known to enhance viscosity (Thole, J., 1914, **105**, 2004).

(*B*) When the groups have considerable residual affinity, the *cis*-isomeride will have the smaller viscosity, because the proximity of the groups is favourable to the *intra*molecular neutralisation of the residual affinities, thus lowering the net residual affinity of the molecule. The *inter*molecular association is consequently decreased and the viscosity of the compound lowered.

Since the hydroxyl group has large residual affinity, it is probable that the *trans*-methyl*cyclo*hexanols will possess the greater viscosities and, also, that the greatest difference will be observed between the viscosities of the isomerides of 2-methyl*cyclo*hexanol, since it is clear that effect *B* will be the more strongly operative the nearer the dominant groups are to each other. These predictions are

borne out by the measurements of the viscosities of the six geometrical isomerides, which are as follows:

Methyl*cyclo*hexanol.	$\eta^{25°}$.	Difference (α- minus β-).
dl-α-2-	0·336	0·181
dl-β-2-	0·155	
dl-α-3-	0·251	0·054
dl-β-3-	0·197	
α-4-	0·385	0·138
β-4-	0·247	

It will also be seen that, in accordance with the " boat " formula for the *cyclo*hexane ring (*vide infra*), the para-substitutents are apparently closer together than the meta-, although not as close as the ortho-.

These measurements were then extended to the methyl*cyclo*hexanyl acetates. The result of converting an alcohol into an acetate—from the point of view of the postulates of Thole—is to reduce the residual affinity of one of the dominant groups, because an acetic ester is almost invariably less viscous than its parent alcohol. Thus, in the series of the six methyl*cyclo*hexanyl acetates, the effect *B* will have less influence than it had in the alcohol series and, indeed, the effect *A* may become dominant in some cases—most likely in the case of the 3-methyl*cyclo*hexanyl acetates where the effect *B* was already weak in the alcohol series.

Measurement of the viscosities of the methyl*cyclo*hexanyl acetates showed that, in the case of the 3-isomerides, the expected reversal of the order of the viscosities takes place.

Methyl*cyclo*hexanyl acetate.	$\eta^{25°}$.	Difference (α- minus β-).
dl-α-2-	0·0233	+0·0022
dl-β-2-	0·0211	
dl-α-3-	0·0174	−0·0021
dl-β-3-	0·0195	
α-4-	0·0217	+0·0021
β-4-	0·0196	

A similar behaviour is shown by the melting points of the derivatives of the 3-methyl*cyclo*hexanols—the α-derivatives having the higher melting point when they contain a free carboxyl group and the lower when they contain no group of high residual affinity.

	Hydrogen phthalic ester.	*p*-Nitrobenzoate.	*p*-Toluenesulphonate.
dl-α-3-Methyl*cyclo*hexanyl ...	M. p. 93—94°	58°	39—40°
dl-β-3-Methyl*cyclo*hexanyl ...	„ 82—83	65	46—47

All the derivatives of α-2-methyl*cyclo*hexanol, and most of the derivatives of α-4-methyl*cyclo*hexanol, have higher melting points than the corresponding β-derivatives.

Each of the above co-relations has been based on the assumption

that the α-compounds possess the *trans*-configuration and since these relations agree amongst themselves, the truth of this assumption becomes probable.

The anomalous results given by cyclic geometrical isomerides which contain the dominant groups in the meta-position has already been noted by Stewart (" Stereochemistry," p. 150, 1907 edn.).

Similar relations appear to exist between the magnitudes of the optical rotatory powers of *l*-α- and *l*-β-3-methyl*cyclo*hexanols and their derivatives, since the β-alcohol and its hydrogen phthalic ester possess higher rotatory powers than those of the corresponding α-compounds, whilst the β-acetic ester has a lower value than the α-acetic ester :

	a_{5893}.	$[\alpha]_{5893}$ hydrogen phthalic ester.	a_{5893} ($l = 0{\cdot}5$) acetic ester.
l-α-3-Methyl*cyclo*hexanol	−1·74°	−13·51°	−10·83°
l-β-3-Methyl*cyclo*hexanol	−3·37	−26·93	− 4·51

l-α-2-Methyl*cyclo*hexanol and its derivatives all possess higher rotatory powers than the corresponding β-compounds.

Four optically inactive isomerides would be expected from each cresol if the configurations of the *cyclo*hexane ring, postulated by Sachse (*Ber.*, 1890, **23**, 1363; *Z. physikal. Chem.*, 1892, **10**, 203; 1893, **11**, 185) exist in a stable state. No evidence, however, of more than two isomerides was obtained by the crystallisation of the solid esters of any of the hydrogenated cresols. Some indication as to which configuration of the ring is present in the compounds examined was obtained in the following way. If the influence of effect *A* on the viscosities of the methyl*cyclo*hexanols is neglected, the difference between the viscosities of the members of any pair of geometrical isomerides should be approximately proportional to the difference of the distances between the methyl and the hydroxyl groups in the *cis*- and in the *trans*-forms. These distances were measured on the " chair " and " boat " models of the different isomerides, the latter giving maximum and minimum values owing to the fact that it possesses transverse rotational movement (compare Wightman, J., 1925, **127**, 1421). The values obtained from the " boat " model are in agreement with the viscosity measurements, but those obtained from the stiff " chair " model are widely at variance. This would tend to show that the " boat " model corresponds to the structure of the majority of the molecules in the substances examined.

(*d*) *The Relative Amounts of the Geometrical Isomerides produced by Different Methods of Preparation.*

The hydrogenation of the cresols by the method of Sabatier and Senderens yielded mixtures containing but small amounts of the

β-isomerides and, since large amounts of these isomerides were required, other methods of preparation were employed. In all cases the percentage proportions of the two isomerides in each of these mixtures (for they all proved to be mixtures) was found by observing the viscosity of a specially purified sample and comparing this value with those on a viscosity–composition diagram which had been previously constructed by determining the viscosities of samples of the pure isomerides mixed in known proportions.

The samples of the reduction products were subjected to a rigid purification before the determination of their viscosities, since the method of estimating the proportions of the two isomerides demands that the samples should be of high purity.

By applying this procedure to the mixtures obtained by the various methods, the following results were obtained:

Method of preparation.	% α-Isomeride.
(i) Hydrogenation of *o*-cresol by Sabatier and Senderens's method at 175° (nickel catalyst)	67
(ii) Reduction of 2-methyl*cyclo*hexanone by sodium and boiling ethyl alcohol	77
(iii) Reduction of 2-methyl*cyclo*hexanone by sodium and moist ether	81
(iv) Reduction of 2-methyl*cyclo*hexanone by Skita's method (platinum catalyst)	38
(v) Hydrogenation of *m*-cresol by Sabatier and Senderens's method at 100°	80
(vi) Hydrogenation of *m*-cresol by Sabatier and Senderens's method at 180°	82
(vii) Reduction of 3-methyl*cyclo*hexanone by sodium and boiling ethyl alcohol	86

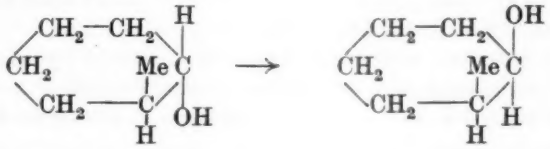
The mixture of methyl*cyclo*hexanols obtained in experiment (iv) was prepared by shaking an aqueous–acetic acid solution of 2-methyl-*cyclo*hexanone containing colloidal platinum in an atmosphere of hydrogen, the instructions given by Skita being closely followed (*loc. cit.*). Since the product was apparently the same as that prepared by Skita (yielding a phenylcarbamate, m. p. 94—96°; Skita gives 95°), it is clear, in view of the result given above, that the substance described by this author as *cis*-2-methyl*cyclo*hexanol is actually a mixture of the *cis*- and *trans*- forms.

(*e*) *The Geometrical Inversion and the Relative Configurations of the Methyl*cyclo*hexanols.*

In a series of preliminary experiments, the methyl*cyclo*hexanols were found to be singularly inert towards reagents which often effect the geometrical inversion of cyclic geometrical isomerides. Thus heating with water at 120° produced no change in the proportion of the geometrical isomerides present in a mixture of α- and β-2-methyl*cyclo*hexanols, and protracted boiling with alcoholic

sodium hydroxide caused but a slight increase in the proportion of α-4-methyl*cyclo*hexanol in a mixture of the α- and β-forms.

It is clear, however, that if the configuration of the carbon atom to which the hydroxyl group is attached could be reversed, a *trans*-methyl*cyclo*hexanol would be converted into the corresponding *cis*-isomeride, thus :—



Hence the valuable method, apparently one of general application, discovered by Phillips (J., 1923, **123**, 43) for reversing the configuration of optically active secondary alcohols seemed adaptable to the present problem. Following this method, the *p*-toluenesulphonic ester of *dl*-α-2-methyl*cyclo*hexanol was prepared and allowed to react with potassium acetate in alcoholic solution. From the products of the reaction a methyl*cyclo*hexanyl acetate was isolated which, on hydrolysis, yielded *dl*-β-2-methyl*cyclo*hexanol apparently uncontaminated with the α-isomeride.

Similar experiments, carried out with *dl*-α-3- and *dl*-α-4-methyl*cyclo*hexanyl *p*-toluenesulphonates, yielded *dl*-β-3- and *dl*-β-4-methyl*cyclo*hexanols. A lævorotatory *l*- + *dl*-α-2-, and *l*-α-3-methyl*cyclo*hexanyl *p*-toluenesulphonates yielded *d*- + *dl*-β-2-, and *l*-β-3-methyl*cyclo*hexanols by a similar treatment.

It has also been found that the reverse transformation can be effected. This has been demonstrated by the formation of *dl*-α-3-methyl*cyclo*hexanol from *dl*-β-3-methyl*cyclo*hexanyl *p*-toluenesulphonate.

The importance of these interconversion experiments in the study of the stereochemistry of the methyl*cyclo*hexanols is considerable, since not only do they provide a ready means of preparing the β-isomerides and a method of determining the relative configurations of the different isomerides, but they also provide a check on the purity of the β-isomerides, which, in some cases, are very difficult to purify.

It will be seen from the diagrams on p. 2053 that the configurational relations between (i) the 2-methyl*cyclo*hexanols and 2-methyl*cyclo*hexanone on the one hand and between (ii) the 3-methyl*cyclo*hexanols and 3-methyl*cyclo*hexanone on the other, represent two different types.

Examples of both these types of relations have been already recorded in this series of communications (Part I, J., 1907, **91**,

1979; Part II, J., 1912, **101**, 109; Part IV, J., 1925, **127**, 1472), although only the type (i) apparently has been recorded elsewhere. In type (i), the same ketone is obtained by oxidation of alcohols of opposite signs of rotatory power—a state of affairs which also exists between *l*-menthol and *d-neo*menthol, which yield *l*-menthone (Part II); between *l*-borneol and *d-iso*borneol, which give *l*-camphor (Part I); and between the tanacetyl alcohols, which yield tanacetone (Tschugaev, *Ber.*, 1912, **45**, 1293).

In (ii), however, the same ketone is obtained by oxidation of alcohols of the same sign of rotatory power, the only other example recorded being *l*-α- and *l*-β-fenchyl alcohols, which give *d*-fenchone on oxidation (Part IV).

EXPERIMENTAL.

(*a*) *The Separation of the Geometrical Isomerides.*

The cresols were hydrogenated at 175° by the method of Sabatier and Senderens at the laboratories of Messrs. Crossfield & Co. *o*-Cresol was found the most difficult to hydrogenate. Some *m*-cresol was also hydrogenated at 100° and at 180° by the Technical Research Works, Ltd., using the special electrolytically prepared nickel catalyst described by Lush (*J. Soc. Chem. Ind.*, 1923, **42**, 219T). To both these firms the authors tender their sincere thanks.

The crude products were fractionally distilled several times through a rod-and-disk column under reduced pressure. Three groups of fractions were collected in each case: methyl*cyclo*hexanones, b. p. 62—64°/20 mm., methyl*cyclo*hexanols, b. p. 77—80°/20 mm., and cresols, b. p. 85—100°/20 mm. The second sets of fractions were separately heated with phthalic anhydride (10% excess) at 110° for 12 hours. The product was then poured, while still liquid, into a slight excess of sodium carbonate solution, the resulting solution filtered, diluted to a large volume with water, and extracted ten times with benzene. The aqueous portion was freed from benzene by the passage of air and the acid ester precipitated by the addition of acid. The ester thus obtained was freed from phthalic acid by dissolving it in chloroform, drying and filtering the solution, and removing the chloroform, first by distillation and finally in a vacuum.

dl-α-2-*Methyl*cyclo*hexanyl Hydrogen Phthalate.*—The mixture of crude esters obtained by the action of phthalic anhydride on hydrogenated *o*-cresol was submitted to fractional crystallisation from glacial acetic acid. Some four to five crystallisations of the principal crop yielded an ester unchanged by further crystallisation from either acetic acid or benzene. dl-α-2-*Methyl*cyclo*hexanyl hydrogen phthalate* thus obtained formed a white, crystalline powder, m. p.

124—125° (0·5121 g. required 0·0783 g. of sodium hydroxide for complete neutralisation. Calc., 0·0783 g.).

dl-α-2-*Methyl*cyclo*hexanol*.—The pure acid ester (1 mol.) was dissolved in a solution of sodium hydroxide (2·2 mols.) in water (five times the weight of ester), and the mixture distilled in a current of steam. The distillate was extracted three times with ether and the united ethereal extracts were dried with potassium carbonate. After the removal of the ether, the residual alcohol was distilled. dl-α-2-*Methyl*cyclo*hexanol*, b. p. 78—79°/20 mm., thus obtained formed a colourless, viscous liquid with an odour reminiscent of that of cocoanut oil.

dl-β-2-*Methyl*cyclo*hexanyl Hydrogen Phthalate*.—The mother-liquors from the preparation of the α-ester were poured into ice-water, and the precipitated ester collected, dried, and crystallised from light petroleum. Pure dl-β-2-*methyl*cyclo*hexanyl hydrogen hthalate* was finally obtained as large, stellate masses, m. p. 89—90° (0·3307 g. required 0·0506 g. of sodium hydroxide for complete hydrolysis. Calc., 0·0505 g.).

The following method was found to possess considerable advantages over that just described for the preparation of a pure *dl*-β-2-methyl*cyclo*hexanyl ester. The hydrogen phthalic esters, recovered from the mother-liquors from the preparation of the α-ester, were hydrolysed, and the resulting alcohols converted into the *p*-nitrobenzoates. By systematic fractional crystallisation of this mixture from methyl alcohol, pure dl-β-2-*methyl*cyclo*hexanyl* p-*nitrobenzoate* m. p. 35—36°, was obtained as light yellow plates.

dl-β-2-*Methyl*cyclo*hexanol* was obtained by the hydrolysis of either the hydrogen phthalic ester or of the *p*-nitrobenzoate. It formed a colourless, viscous liquid, b. p. 77—78°/20 mm., and possessed an odour indistinguishable from that of its geometrical isomeride.

α-4-*Methyl*cyclo*hexanyl hydrogen phthalate* was obtained by the crystallisation, from glacial acetic acid, of the mixture of hydrogen phthalic esters formed by the action of phthalic anhydride on hydrogenated *p*-cresol. Five crystallisations of the principal crop yielded pure α-4-*methyl*cyclo*hexanyl hydrogen phthalate*, m. p. 119—120° (0·3007 g. required 0·0461 g. of sodium hydroxide for complete neutralisation. Calc., 0·0458 g.).

α-4-*Methyl*cyclo*hexanol*, b. p. 78—79°/20 mm., was obtained from the corresponding hydrogen phthalic ester in the usual way and possessed an odour similar to, although distinct from, that of the 2-methyl*cyclo*hexanols.

β-4-*Methyl*cyclo*hexanyl Hydrogen Phthalate*.—The hydrogen phthalic esters recovered from the mother-liquors from the pre-

paration of the α-ester were crystallised from light petroleum. After many crystallisations, β-4-*methyl*cyclo*hexanyl hydrogen phthalate*, m. p. 72—73°, was obtained as a white, crystalline powder, unaltered in melting point by further crystallisation. This substance was found very difficult to isolate in a pure condition (0·3150 g. required 0·0481 g. of sodium hydroxide for complete neutralisation. Calc., 0·0482 g.).

β-4-*Methyl*cyclo*hexanol*, b. p. 78—79°/20 mm., was obtained from the hydrogen phthalic ester in the usual manner and possessed an odour similar to that of the α-isomeride.

dl-α-3-*Methyl*cyclo*hexanyl* p-*Nitrobenzoate*.—It was found impossible to purify the mixture of hydrogen phthalic esters resulting from the action of phthalic anhydride on hydrogenated *m*-cresol; the corresponding mixture of *p*-nitrobenzoic esters, however, can be readily separated into its components by crystallisation from methyl alcohol. This mixture was prepared by treating hydrogenated *m*-cresol (1 mol.; purified from 3-methyl*cyclo*hexanone and unchanged cresol) with a solution of *p*-nitrobenzoyl chloride (1 mol.) in benzene (8 volumes). Much heat was evolved, but the temperature was kept below 40°. After standing over-night, the mixture was repeatedly washed with water, with dilute hydrochloric acid, and with sodium carbonate solution. The benzene layer was distilled in a current of steam, and the residue of 3-methyl*cyclo*hexanyl *p*-nitrobenzoates, which solidified on cooling, was separated and dried. Crystallisation of these esters from methyl alcohol yielded two sets of crops, each of which was unchanged in melting point by further crystallisation from methyl alcohol, light petroleum, or acetone.

dl-α-3-*Methyl*cyclo*hexanyl* p-*nitrobenzoate* crystallised in well-formed, light yellow granules, m. p. 58°. dl-β-3-*Methyl*cyclo*hexanyl* p-*nitrobenzoate* separated in flat, feathery crystals, m. p. 65°. The corresponding alcohols were obtained by hydrolysis of these esters by means of a slight excess of alcoholic sodium hydroxide (considerable darkening, owing to the partial reduction of the nitrobenzoic acid, takes place if a large excess is employed). dl-α-3-*Methyl*cyclo*hexanol*, b. p. 77—78°/20 mm., and dl-β-3-*methyl*cyclo*hexanol*, b. p. 77—78°/20 mm., obtained in this way, formed colourless, viscous liquids both possessing odours stronger and sweeter than those of the 2- or the 4-methyl*cyclo*hexanols.

dl-α-3-*Methyl*cyclo*hexanyl hydrogen phthalate* was obtaind in the usual manner and formed a white, crystalline power, m. p. 93—94° (0·2111 g. required 0·0323 g. of sodium hydroxide for complete neutralisation. Calc., 0·0322 g.).

dl-β-3-*Methyl*cyclo*hexanyl hydrogen phthalate* formed white

crystals, m. p. 82—83° (0·321 g. required 0·0488 g. of sodium hydroxide for complete neutralisation. Calc., 0·0490 g.).

The β-*eucaine* salts of the complete series of six optically inactive methyl*cyclo*hexanyl hydrogen phthalates were prepared by mixing an aqueous solution of the sodium salt of the hydrogen phthalic ester with an equimolecular amount of β-eucaine hydrochloride dissolved in water. The supernatant liquid was decanted and the residual gum crystallised from aqueous alcohol. In no case was the melting point of the salt found to change on repeated crystallisation.

β-Eucaine salt of	M. p.
dl-α-2-methyl*cyclo*hexanyl hydrogen phthalate	173—174°
dl-β-2- ,, ,, ,, ,, ...	154
dl-α-3- ,, ,, ,, ,, ...	149—150
dl-β-3- ,, ,, ,, ,, ...	171—172
α-4- ,, ,, ,, ,, ...	170—171
β-4- ,, ,, ,, ,, ...	170—171

The *methyl*cyclo*hexanyl phenylcarbamates* were prepared by allowing equimolecular amounts of the methyl*cyclo*hexanol and phenylcarbimide to stand in a closed vessel for a day. Since these compounds were used in conjunction with viscosity, to characterise a mixture of methyl*cyclo*hexanols, the resulting solid mass was crystallised once only from light petroleum. The melting points of these derivatives are in Table I.

(*b*) *The Optically Active Forms of the Geometrical Isomerides of* 2- *and of* 3-*Methyl*cyclo*hexanol.*

The d- *and* l-2-*Methyl*cyclo*hexanols.*—*dl*-α-2-Methyl*cyclo*hexanyl hydrogen phthalate gave with strychnine a crystalline salt, m. p. 190°, which after systematic fractional crystallisation yielded, on decomposition, a small amount of acid ester showing $[\alpha]_{5893}$ −52·2° in benzene ($c = 5{\cdot}00$; $l = 2$). Since the salt decomposed easily into the alkaloid and the acid ester in acetone solution, optical purity could not be obtained in this manner. Ethyl alcohol was then substituted for acetone as a solvent; but whilst this prevented decomposition, the rapidity of the resolution decreased enormously. After the trial of some other alternatives, the following process was adopted: the strychnine salt of the inactive ester was crystallised once from ethyl alcohol and the crop and the mother-liquor were decomposed, yielding esters with approximately $[\alpha]_{5893} \pm 17°$. These esters were then separately crystallised from acetic acid; the ester which crystallised was almost inactive, whilst the mother-liquors yielded esters having approximately $[\alpha]_{5893} \pm 48°$. The united inactive esters were then recombined with strychnine and

the above process was repeated until about 100 g. of the esters with $[\alpha]_{5893}$ + 48° and − 48° had been collected. Recombination of each of these sets of esters with strychnine gave, after many crystallisations from acetone, esters unaltered in rotatory power by further crystallisation of their strychnine salts from acetone or from ethyl alcohol.

d-α-2-*Methyl*cyclo*hexanyl hydrogen phthalate*, m. p. 122—123°, obtained in this way had $[\alpha]_{5893}$ + 63·2° in benzene ($c = 2{\cdot}84$; $l = 2$).

l-α-2-*Methyl*cyclo*hexanyl hydrogen phthalate*, m. p. 122°, had $[\alpha]_{5893}$ −63·5° under the same conditions.

d-α-2-*Methyl*cyclo*hexanol*, b. p. 78°/20 mm., and l-α-2-*methyl*-cyclo*hexanol*, b. p. 78°/20 mm., were obtained from the corresponding hydrogen phthalic esters in the usual manner.

d- *and* l-β-2-*Methyl*cyclo*hexanols*.—The resolution of *dl*-β-2-methyl *cyclo*hexanyl hydrogen phthalate into its optically active components was found to be very difficult; after many preliminary experiments, the following process was adopted: the inactive ester was combined with *l*-α-phenylethylamine, and the resulting salt crystallised many times from acetone; 35% of the total ester was thus obtained with $[\alpha]_{5461}$ −19°, and this, on combination with strychnine, yielded a salt which rapidly attained optical purity when crystallised from acetone. l-β-2-*Methyl*cyclo*hexanyl hydrogen phthalate*, m. p. 97—98°, obtained from this salt, had $[\alpha]_{5461}$ −46·8° and $[\alpha]_{5893}$ −38·7° in benzene ($c = 5{\cdot}00$; $l = 2$).

The acid ester obtained from the mother-liquors of the above crystallisations, after being crystallised from light petroleum, yielded a fraction with $[\alpha]_{5461}$ + 22·1°. Recrystallisation of the strychnine salt of this ester from acetone gave the strychnine salt of d-β-2-*methyl*cyclo*hexanyl hydrogen phthalate*. The ester obtained from this salt had $[\alpha]_{5461}$ + 46·1° in benzene ($c = 5$; $l = 2$).

l-β-2-*Methyl*cyclo*hexanol*, b. p. 78—79°/29 mm., was obtained from the corresponding ester in the usual manner. The determined physical properties of this compound together with those of d-β-2-*methyl*cyclo*hexanol* which was obtained from the ester, are in Table II.

It is noteworthy that in the resolution of the α-isomeride by the use of strychnine, the *d*-form separates from acetone solution first, whereas, in the resolution of the β-isomeride, the *l*-form separates first. This, indeed, is to be expected, since it is shown in this communication that the *d*-α-isomeride is similar in configuration to the *l*-β-isomeride.

On oxidation by the method of Beckmann (*Annalen*, 1889, **250**, 325), *l*-α-2-methyl*cyclo*hexanol was converted into l-2-*methyl*cyclo-

hexanone, b. p. 59—60°/20 mm., showing $[\alpha]^{25°}_{4359}$ −43·0°, $[\alpha]^{25°}_{5461}$ −18·91°, and $[\alpha]^{25°}_{5893}$ −15·22° ($l = 0·5$); $d^{25°}_{4°}$ 0·9230.

This ketone rapidly racemised when treated with cold alcoholic sodium hydroxide, probably owing to passage through the symmetrical *enol*-tautomeride :

$$CH_2\langle\begin{matrix}CH_2\text{——}CH_2\\CH_2\text{—}C(OH)\end{matrix}\rangle C\cdot Me$$

Stable esters of the *enolic* form of 2-methyl*cyclo*hexanone have been prepared by Murat (*Ann. Chim.*, 1909, **16**, 108).

l-β-2-Methyl*cyclo*hexanol yielded, in a similar manner, a ketone with $[\alpha]^{18°}_{5893}$ + 14·21° ($l = 0·5$), $d^{18°}_{4°}$ 0·9262.

l-α- *and* l-β-3-*Methyl*cyclo*hexanols*.—*d*-3-Methyl*cyclo*hexanone, b. p. 72°/25 mm., $\alpha^{25°}_{5893}$ + 10·6°, was obtained from pulegone by the method described by Rupe (*Annalen*, 1924, **436**, 184).

This ketone (1 mol.) mixed with ether (10 vols.) was poured on to sodium (3 atoms), and small quantities of water were added from time to time. After dissolution of the sodium, the separated ethereal layer was repeatedly washed with sodium bisulphite solution and with water, dried with potassium carbonate, the ether removed, and the residue distilled. A mixture of 3-methyl*cyclo*hexanols, b. p. 78—79°/20 mm., was thus obtained with $\alpha^{24°}_{5461}$ −3·58° (yield 80%). A residue of viscid, fluorescent oil remained in the flask.

Six crystallisations of the *p*-nitrobenzoic ester of this alcohol yielded l-α-3-*methyl*cyclo*hexanyl* p-*nitrobenzoate*, unchanged by further crystallisation either in melting point or in optical rotatory power ($[\alpha]_{5461}$ −3·8° in methyl alcohol, $c = 5·00$; $l = 2$; m. p. 45·5—46·5°) (Found : N, 5·4. $C_{14}H_{17}O_4N$ requires N, 5·3%).

l-α-3-*Methyl*cyclo*hexanol*, b. p. 78—79°/20 mm., obtained by the hydrolysis of this ester had $[\alpha]^{26·5°}_{5461}$ −4·22°, $d^{26·5°}_{4°}$ 0·9131, and $\eta^{25°}$ 0·251. When oxidised with chromic acid, it gave *d*-3-methyl*cyclo*hexanone, b. p. 66—67°/25 mm., with $\alpha^{21°}_{5893}$ + 11·54° ($l = 1$). *l*-β-3-Methyl*cyclo*hexanol, the preparation of which is described in the next section, yielded in a similar manner a ketone, b. p. 56—57°/14 mm., with $\alpha^{17°}_{5893}$ + 11·64°.

l-α-3-*Methyl*cyclo*hexanyl hydrogen phthalate*, m. p. 94—95°, obtained from the corresponding alcohol in the usual manner, had $[\alpha]^{19°}_{5461}$ −17·39° and $[\alpha]^{19°}_{5893}$ −13·51° in benzene ($c = 5·01$; $l = 2$).

The *methyl*cyclo*hexanyl acetates*, prepared by warming the alcohols with an excess of acetic anhydride on the water-bath for 2 hours, are colourless, mobile liquids possessing sharp, pleasant odours. The particular character of the odour varies rather markedly throughout the series.

TABLE I.

Methyl*cyclo*hexanyl acetate.	B. p. /20 mm.	$d_4^{25°}$.	$n_{5893}^{25°}$.	$[R_L]_{5893}^{25°}$.	$\eta^{25°}$.
dl-α-2-	79—80°	0·9430	1·4389	43·48	0·0233
dl-β-2-	79—80	0·9434	1·4376	43·34	0·0211
dl-α-3-	81—82	0·9454	1·4313	43·94	0·0174
dl-β-3-	78—79	0·9430	1·4369	43·38	0·0195
α-4-	78—80	0·9380	1·4373	43·46	0·0217
β-4-	78—79	0·9337	1·4365	43·75	0·0196
Methyl*cyclo*hexanol.					
dl-α-2-	77—79	0·9228	1·4596	33·81	0·336
dl-β-2-	77—78	0·9228	1·4616	33·93	0·155
dl-α-3-	78—79	0·9104	1·4530	33·87	0·251
dl-β-3-	77—78	0·9091	1·4554	34·01	0·197
α-4-	78—79	0·9080	1·4544	34·02	0·385
β-4-	78—79	0·9180	1·4584	33·91	0·247

$[R_L]_{5893}$ calc., 33·85 (Eisenlohr's figures).

	M. p. of				
Methyl*cyclo*hexanol.	hydrogen phthalate.	phenyl-carbamate.	*p*-nitro-benzoate.	hydrogen succinate.	*p*-toluene-sulphonate.
dl-α-2-	124—125°	105—106°	65°	44—46°	27—28°
dl-β-2-	89— 90	78— 80	35—36	30—31	—
dl-α-3-	93— 94	92— 93	58	Oil.	39—40
dl-β-3-	82— 83	101—103	65	—	46—47
α-4-	119—120	124—125	67	—	71—72
β-4-	72— 73	124	94	—	—

(*c*) *The Methyl*cyclo*hexanyl* p-*Toluenesulphonates.*

The solid mass produced by the interaction of finely powdered *p*-toluenesulphonyl chloride (1·02 mols.) and a solution of the methyl*cyclo*hexanol in pyridine (1·05 mols.) was ground under water, washed many times with dilute hydrochloric acid and water, dried, and crystallised from light petroleum.

All the members of this series of esters formed white, wax-like crystals which decomposed at about 160° with the evolution of a volatile substance (methyl*cyclo*hexenes). Unlike menthyl *p*-toluenesulphonate, which reacts almost immediately with aromatic amines to give menthene and the amine toluenesulphonate (Ferns and Lapworth, J., 1912, **101**, 273), the methyl*cyclo*hexanyl toluenesulphonates react only very slowly with aniline. The melting points of these derivatives are in Table I (the quantities of sodium hydroxide required for the complete hydrolysis of 1·0081 g. of the *dl*-α-2-ester, 1·0092 g. of the *dl*-α-3-ester, 1·0042 g. of the α-4-ester, and 1·0857 g. of the *l*-α-3-ester were 0·151, 0·150, 0·146, and 0·162 g. respectively. Calc.: 0·148, 0·149, 0·148, and 0·162 g.).

l-α-3-*Methyl*cyclo*hexanyl* p-*toluenesulphonate*, m. p. 36—37°, had $[\alpha]_{5461}^{19°}$ — 26·3° and $[\alpha]_{5893}^{19°}$ —21·0° in benzene ($c = 5·018$; $l = 2$).

In the following experiments a part only of the sulphonic ester was converted into carboxylic ester, and only this part was considered in calculating the percentage inversion referred to, which is the percentage conversion of an α-methyl*cyclo*hexanol into a β-methyl*cyclo*hexanol (or *vice versa*).

(i) *dl*-α-2-Methyl*cyclo*hexanyl *p*-toluenesulphonate (1 mol.), ethyl alcohol (1·5 times the volume of the molten sulphonic ester), and potassium acetate (4 mols.) were heated on the water-bath for 24 hours. The mixture was then poured into water, neutralised with sodium carbonate, and extracted five times with ether. The ether was removed from the dried ethereal extracts and the residue was distilled, first under ordinary pressure and finally under reduced pressure. In this manner were obtained a mixture of ethyl acetate and methyl*cyclo*hexene, b. p. 75—80/760 mm.; methyl*cyclo*hexene, b. p. 104—115°/760 mm.; methyl*cyclo*hexanyl ethyl ether b. p. 65—70°/20 mm., and 2-methyl*cyclo*hexanyl acetate, b. p. 76—81°/20 mm. The first fractions, freed from ethyl acetate by washing with water, yielded methyl*cyclo*hexene, b. p. 104—105°, $d_4^{18°}$ 0·8077, $d_4^{22°}$ 0·8052, $d_4^{26°}$ 0·8023, and $n_{5893}^{18°}$ 1·4409, whence $[R_L]_{5893}$ 31·41; calc., 31·76 (compare Wallach, *Ber.*, 1902, **35**, 2822; Markovnikov and Stadnikov, *J. Russ. Phys. Chem. Soc.*, 1903, **35**, 389; Markovnikov and Tscherdintzev, *ibid.*, 1900, **32**, 302).

After repeated fractionation the third fraction yielded 2-methyl*cyclo*hexanyl ethyl ether, b. p. 69—70°/21 mm., $n_{5893}^{20°}$ 1·4701, $d_4^{20°}$ 0·922, whence $[R_L]_{5893}$ 43·5; calc., 43·4 (compare Murat, *loc. cit.*).

The ester fraction gave a methyl*cyclo*hexanyl acetate, b. p. 78—80°/20 mm., $d_4^{25°}$ 0·9432, $n_{5893}^{25°}$ 1·4382, which, after hydrolysis with alcoholic sodium hydroxide, yielded a methyl*cyclo*hexanol. After purification by conversion into the hydrogen phthalic ester, this substance was shown to be *dl*-β-2-methyl*cyclo*hexanol with $d_4^{25°}$ 0·9226 and $\eta^{25°}$ 0·155.

The hydrogen phthalic ester, obtained from this alcohol in the usual manner, had m. p. 89—90°, which was not depressed by admixture of the *dl*-β-2-methyl*cyclo*hexanyl hydrogen phthalate previously prepared from *o*-cresol.

The yield of ester was 25%, of ether 20%, and of methyl*cyclo*hexene 40%.

(ii) *dl*-α-2-Methyl*cyclo*hexanyl *p*-toluenesulphonate was mixed with ammonium acetate (3 parts), and ethyl alcohol added until the whole formed a solution at 80°. After being heated for 18 hours on the water-bath, the mixture was worked up in a similar manner to that described above. The yields of methyl*cyclo*hexanyl acetate, methyl*cyclo*hexene, and methyl*cyclo*hexanyl ethyl

ether were 70%, 15%, and 5% respectively. 2-Methyl*cyclo*hexanol obtained from the ester had $\eta^{25°}$ 0·180, whence the estimated inversion is 85%.

(iii) *dl*-α-2-Methyl*cyclo*hexanyl *p*-toluenesulphonate, mixed with benzene (7·5 vols.) and formic acid (anhydrous; 1·5 vols.), was heated for 18 hours on the water-bath. 2-Methyl*cyclo*hexanyl formate and methyl*cyclo*hexene were obtained each in 40% yield. On hydrolysis the former yielded 2-methyl*cyclo*hexanol with $\eta^{25°}$ 0·246, whence the estimated inversion is 40%.

(iv) *dl*-α-2-Methyl*cyclo*hexanyl *p*-toluenesulphonate, mixed with formamide (2·5 vols.) and formic acid (3·5 vols.), was heated for 18 hours on the water-bath. 2-Methyl*cyclo*hexanyl formate was obtained in 45% yield, and methyl*cyclo*hexene in 40% yield. The formic ester yielded 2-methyl*cyclo*hexanol with $\eta^{25°}$ 0·232 whence the inversion is 50%.

A similar experiment in which the formamide was replaced by water yielded ultimately 2-methyl*cyclo*hexanol with $\eta^{25°}$ 0·232, whence the inversion is 50%.

(v) *dl*-α-2-Methyl*cyclo*hexanyl *p*-toluene sulphonate, mixed with glacial acetic acid (5 vols.) and potassium acetate (equal in weight to the ester), was heated for 1 day on the water-bath. 2-Methyl*cyclo*hexanyl acetate was obtained in 50% yield, and methyl*cyclo*hexene in 30% yield. The acetic ester gave 2-methyl*cyclo*hexanol with $\eta^{25°}$ 0·180, whence the inversion is 82%.

(vi) *dl*-α-3-Methyl*cyclo*hexanyl *p*-toluenesulphonate was allowed to react with potassium acetate under the conditions described in experiment (i). 3-Methyl*cyclo*hexanyl acetate was obtained in 20% yield, 3-methyl*cyclo*hexanyl ethyl ether in 5% yield, and methyl*cyclo*hexene in 60% yield. The *dl*-β-3-methyl*cyclo*hexanol ultimately obtained with $\eta^{25°}$ 0·196 gave a phenylcarbamate, the m. p. of which, 101—102°, was not depressed by admixture of the previously prepared *dl*-β-3-methyl*cyclo*hexanyl phenylcarbamate. Thus the inversion is complete as far as the experimental methods used are capable of indicating it.

(vii) α-4-Methyl*cyclo*hexanyl *p*-toluenesulphonate was allowed to react with potassium acetate under the conditions described in (i). 4-Methyl*cyclo*hexanyl acetate was obtained in 30% yield, 4-methyl*cyclo*hexanyl ethyl ether in 10% yield, and methyl*cyclo*hexene in 40% yield. The ester yielded, on hydrolysis, β-4-methyl*cyclo*hexanol with $\eta^{25°}$ 0·247. The hydrogen phthalic ester derived from this alcohol had m. p. 72°, which was not depressed by the admixture of the β-4-methyl*cyclo*hexanyl hydrogen phthalate prepared directly from *p*-cresol. Thus the inversion is probably complete.

(viii) *l*-α-3-Methyl*cyclo*hexanyl *p*-toluenesulphonate was allowed to

react with potassium acetate under the conditions described in (i). 3-Methyl*cyclo*hexanyl acetate was obtained in 20% yield, 3-methyl-*cyclo*hexanyl ethyl ether in 5% yield, and methyl*cyclo*hexene in 60% yield. *l*-β-3-Methyl*cyclo*hexanol, $\eta^{25°}$ 0·196, was obtained by the hydrolysis of the ester.

l-β-3-*Methyl*cyclo*hexanyl hydrogen phthalate*, m. p. 70—71°, obtained from the above alcohol in the usual manner, had $[\alpha]^{19°}_{5461}$ −32·7° and $[\alpha]^{19°}_{5893}$ −26·81° in benzene ($c = 5{\cdot}01$; $l = 2$).

The methyl*cyclo*hexene obtained in this experiment, after purification by means of sodium, had b. p. 104—105°, $d^{25°}_{4°}$ 0·7950, and $n^{26°}_{5893}$ 1·4408; whence $[R_L]_{5893}$ 31·88; calc., 31·76. The following determinations of rotatory power were made ($t = 26°$; $l = \frac{1}{2}$): α_{4359} + 88·75°; α_{5461} + 50·86°; α_{5790} + 44·62°; α_{5893} + 42·67°; α_{6708} + 31·99°.

(ix) *dl*-β-3-Methyl*cyclo*hexanyl *p*-toluenesulphonate was allowed to react with potassium acetate under the conditions employed in (i). *dl*-α-3-Methyl*cyclo*hexanol with $\eta^{25°}$ 0·249 was finally obtained.

(x) *d*-+*dl*-α-2-Methyl*cyclo*hexanyl *p*-toluenesulphonate (prepared from *d*-+*dl*-α-2-methyl*cyclo*hexanol, $\alpha^{17°}_{5893}$ + 17·77°, $l = 1$) showed $\alpha^{17°}_{5893}$ + 17·51° ($l = 1$) in the supercooled state. The reaction between this ester and potassium acetate under the conditions employed in (i) yielded ultimately *l*-+*dl*-β-2-methyl*cyclo*hexanol with $\alpha^{20°}_{5893}$ −2·08°, methyl*cyclo*hexanyl ethyl ether with $\alpha^{20°}_{5893}$ + 9·16°, and methyl*cyclo*hexene with $\alpha^{27°}_{5893}$ −22·8°.

(*d*) *Physical Measurements.*

Viscosity.—The type of viscometer used in these determinations was the modification of the Ostwald pattern designed by Thole (J., 1910, **97**, 2596; 1913, **103**, 22) for the measurement of the viscosity of liquids of which only small quantities are available. Two instruments were used, one with a time of flow suitable for the measurement of the viscosities of the methyl*cyclo*hexanols, which was generously provided by Dr. Thole, and the other, with a narrower capillary, for the less viscous methyl*cyclo*hexanyl acetates.

The first instrument was calibrated with *cyclo*hexanol (Thole, J., 1914, **105**, 2011) and *l-iso*propyl-*n*-octylcarbinol (Dunstan and Thole, J., 1913, **103**, 130), and the second with nitrobenzene (Thole, *Z. physikal. Chem.*, 1910, **74**, 684) and with ethyl alcohol (Thole, J., 1914, **105**, 2004).

In addition to the usual precautions taken in determining viscosity, it was found necessary to distil the alcohols and their acetic esters under reduced pressure before each determination and to repeat this process, rejecting the first few drops, until approximately constant values were obtained; otherwise, owing to traces of absorbed

water, no reliance could be placed in the results. The viscosity of a sample of methyl*cyclo*hexanol which had been kept for 8 months in a stoppered bottle, fell 30% but regained the normal value upon distillation. In no case was the observed time of flow less than 150 seconds.

The following viscosities of mixtures of *dl*-β-2- and *dl*-α-2-methyl*cyclo*hexanol were determined; *a* is the percentage of the latter alcohol:

a ...	100	81·2	74·6	66	60·8	60·5	47	25	0
$\eta^{25°}$	0·336	0·313	0·287	0·268	0·255	0·247	0·225	0·185	0·155

The rotatory powers of the methyl*cyclo*hexanols and of their acetic esters were determined in a jacketed tube ($l = 0{\cdot}5$), round which hot oil was circulated for the readings at the higher temperatures. The light sources used were the sodium and lithium flame and the enclosed mercury arc. Densities were determined in a pyknometer of about 1·5 c.c. capacity.

Table II.

Determinations of the Density (d_4^t) *and the Rotatory Power* (α 50 mm.) *of Compounds in the Homogeneous State.*

d-α-2-*Methyl*cyclo*hexanol.*

		α for λ =				
t.	d_4^t.	6708.	5893.	5790.	5461.	4359.
20·5°	0·9271	+13·01°	+17·19°	+17·96°	+20·28°	+34·00°
48	0·9010	12·51	16·66	17·43	19·79	33·30
69	0·8810	12·30	16·31	17·00	19·28	32·60
95	0·8560	12·11	15·91	16·53	18·71	31·70

$a^{30·5°}$ + 36° for λ 4220; + 39° for λ 4146; + 41° for λ 4046; + 43° for λ 3978; + 47° for λ 3820.

l-α-2-*Methyl*cyclo*hexanol.*

$a^{20°}$ − 13·05° for λ 6708; − 17·81° for λ 5893; − 17·95° for λ 5790; − 20·32° for λ 5461; − 34·13° for λ 4359.

l-β-2-*Methyl*cyclo*hexanol.*

		α for λ =				
t.	d_4^t.	6708.	5893.	5790.	5461.	4359.
20°	0·9272	−4·62°	−6·23°	−6·41°	−7·26°	−11·96°
49	0·9009	3·97	5·32	5·48	6·35	10·24
95	0·8560	3·08	4·09	4·24	4·81	7·98
112	0·8519	2·77	3·68	3·82	4·32	7·21
130	0·8220	2·49	3·31	3·43	3·87	6·46

l-α-3-*Methyl*cyclo*hexanol.*

d_4^t 0·9143 at 20°; 0·8919 at 51°; 0·8672 at 85°; 0·8303 at 121°.

(Owing to the small rotatory power of this compound, the determinations made in a 0·5 dcm. tube were untrustworthy and hence determinations were made in a 2 dcm. tube at 20°.)

a_{6708} − 5·41°; a_{5893} − 7·17°; a_{5790} − 7·59°; a_{5461} − 8·48°; a_{4359} − 14·03°.

TABLE II (*continued*).

l-β-3-*Methyl*cyclo*hexanol*.

		α for λ =				
t.	$d_4^{t°}$.	6708.	5893.	5790.	5461.	4359.
16·5°	0·9245	−2·53°	−3·37°	−3·63°	−4·06°	−6·58°
50	0·8991	2·23	2·91	3·10	3·45	5·64
75	0·8774	2·02	2·64	2·78	3·08	5·01
96	0·8551	1·72	2·23	2·35	2·76	4·37
119	0·8389	1·47	1·95	1·97	2·23	3·55
		l-α-2-*Methyl*cyclo*hexanyl Acetate*.				
20	0·9458	−19·27	−25·42	−26·47	−29·96	−49·87
49	0·9221	18·42	24·31	25·36	28·82	47·98
66	0·9072	18·18	24·08	24·81	28·11	46·65
90	0·8851	17·35	22·88	24·05	27·28	45·50
112	0·8624	16·92	22·32	23·27	26·32	43·95
129	0·8478	16·32	21·52	22·62	25·61	42·80
		l-β-2-*Methyl*cyclo*hexanyl Acetate*.				
20	0·9454	−9·11	−12·38	−12·81	−14·50	−25·88
52	0·9202	8·61	11·63	12·20	13·90	24·41
90	0·8848	7·85	10·65	11·13	12·66	22·33
108	0·8681	7·40	10·04	10·42	11·93	21·04
126	0·8509	7·24	9·62	10·10	11·35	19·72
		l-α-3-*Methyl*cyclo*hexanyl Acetate*.				
16	0·9511	−8·13	−10·83	−11·34	−12·82	−21·69
49	0·9262	7·67	10·50	10·87	12·29	20·90
71	0·9071	7·60	10·05	10·54	11·94	20·22
90	0·8903	7·27	9·64	10·19	11·60	19·57
109	0·8724	7·17	9·63	9·87	11·35	19·22
125	0·8549	6·98	9·29	9·79	10·94	18·87
		l-β-3-*Methyl*cyclo*hexanyl Acetate*.				
20	0·9448	−3·40	−4·51	−4·67	−5·30	−8·78
52	0·9197	3·31	4·30	4·45	5·10	8·30
77	0·8974	3·25	4·10	4·26	4·86	7·85
90	0·8849	3·15	3·91	4·07	4·72	7·54
109	0·8671	2·94	3·69	3·88	4·41	7·14
125	0·8502	2·70	3·48	3·66	4·10	6·70

Some of the preliminary work on the separation of the methyl-*cyclo*hexanols was carried out at various times during 1907 and 1912 by Messrs W. O. Littlebury and W. Wilde and Miss H. S. de Pennington, to whom the authors desire to express their thanks. The authors are also indebted to the Government Grant Committee of the Royal Society for a grant which defrayed a part of the expense of this investigation, and two of them (G. A. C. G. and H. H.) gratefully acknowledge receipt of grants from the Department of Scientific and Industrial Research for part of the time during which the work was in progress.

BATTERSEA POLYTECHNIC, S.W. 11. [*Received, May 3rd*, 1926.]

CCLXXVII.—*Piperitone. Part VIII. The Condensation of Piperitone with Aldehydes.*

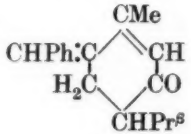
By JOHN CAMPBELL EARL and JOHN READ.

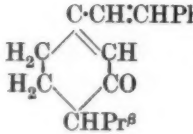
THE ease with which piperitone undergoes condensation with benzaldehyde (J., 1921, **119**, 784) suggested an extension of the reaction to other aldehydes, more especially in view of the striking nature of the dimorphism exhibited by the optically inactive benzylidene derivative (J., 1922, **121**, 574), which appeared to merit further study. In the present communication it is shown that piperitone condenses equally readily with anisaldehyde and also with piperonal. The resulting derivatives, owing to the great facility with which they crystallise, are even more suitable than benzylidene-*dl*-piperitone for the identification of the ketone. Piperitone also undergoes condensation with salicylaldehyde and with opianic acid in a similar manner. In no case, however, was dimorphism evident on the part of the product. Owing to the racemisation of the optically active ketone when condensed with aldehydes in presence of alkali, attempts were also made to effect the reaction in an acid medium, in the hope that the corresponding optically active derivatives might result in this way, a crystallographic examination of the optically active benzylidene derivatives being particularly desirable on account of the exceptional characteristics of benzylidene-*dl*-piperitone. Although condensation was successfully accomplished in this manner, the process was still accompanied by complete racemisation. The condensing action of aqueous hydrochloric acid on mixtures of piperitone with aldehydes seems to be general, but the yields are small. Since neither of these methods of condensation furnished an optically active product, the opianylidene derivative was prepared with the ultimate aim of achieving the optical resolution of the acidic product by means of an optically active base; the salts so far examined, however, show little tendency to crystallise.

As regards the constitution of these piperitone derivatives, it was originally suggested by Simonsen (J., 1921, **119**, 1648) that condensation with benzaldehyde occurs in the 6-position (formula I), owing to the activation exerted by the adjacent ethylenic linking. This suggestion was adopted in a subsequent discussion of the constitution of piperitone (Read, Smith, and Hughesdon, J., 1924, **125**, 129), although for the purpose of the argument it was unnecessary to decide whether condensation actually affects position 6 or position 7. A further study of this question has now indicated that condensation occurs, in fact, in position 7, and not in position 6.

The reaction, however, may still be attributed to the activating influence of the Δ^1-ethylenic linking of piperitone, or, more precisely, to the system C:C·CO, which thus seems to exert its maximum effect in the side chain rather than in the ring. The constitution (II) now advanced for benzylidenepiperitone is based upon the observation that when carefully oxidised with a cold solution of potassium permanganate in acetone this substance yields α-*iso*propylglutaric acid, instead of *iso*propylsuccinic acid as required by formula (I). In the latter case, the production of α-*iso*propylglutaric acid would be possible only by virtue of a simultaneous removal of the benzylidene group by hydrolysis, a process which is extremely unlikely in view of the nature of the reagent and the great stability of benzylidenepiperitone towards hydrolysing agents (J., 1922, **121**, 577). The presumed 6-benzylidene-*dl*-piperitone, 6-benzyl-*dl*-*iso*menthone, 6-benzyl-*dl*-*iso*menthol and 2-benzylidene-6-benzyl-*dl*-*iso*menthone (J., 1924, **125**, 134) must accordingly be regarded as 7-benzylidene-*dl*-piperitone (II), 7-benzyl-*dl*-*iso*menthone, 7-benzyl-*dl*-*iso*menthol, and 2-benzylidene-7-benzyl-*dl*-*iso*menthone, respectively.

(I.)

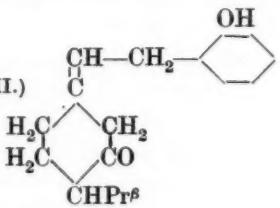


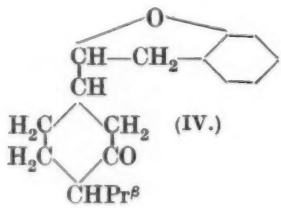


(II.)

Since similar considerations may be applied to the products of condensation of piperitone with other aldehydes, formed in the ways now described, the two isomeric dihydro-derivatives of salicylidenepiperitone mentioned in the experimental part of this paper are probably to be formulated as follows, (III) being soluble and (IV) insoluble in aqueous alkali.

(III.)





(IV.)

EXPERIMENTAL.

Anisylidene-dl-*piperitone*, $C_{10}H_{14}O$:CH·C_6H_4·OMe.—*dl*-Piperitone (10 g.) and anisaldehyde (9 g., 1 mol.) were dissolved in absolute alcohol (20 c.c.) and mixed with a cold solution of sodium (0·4 g., 0·25 mol.) in absolute alcohol (20 c.c.). After keeping for a week,

the solution was poured into an excess of water and made slightly acid with sulphuric acid. The ensuing oily separation of anisylidene-*dl*-piperitone solidified in a few minutes to a crystalline mass (12·8 g.). The derivative is readily soluble in chloroform or benzene, and somewhat less soluble in alcohol or warm ligroin. When recrystallised from alcohol it forms pale yellow crystals, m. p. 98°. No dimorphism was observed after repeated recrystallisation under different conditions (Found: C, 80·1; H, 8·2. $C_{18}H_{22}O_2$ requires C, 79·9; H, 8·25%). The appended crystallographic report was kindly supplied by Dr. Marie Bentivoglio, of the Department of Geology, University of Sydney:

The crystals, which are doubly terminated, vary in habit, being either long prisms—elongated in the direction of the *c* axis—or short crystals equally developed in the directions of the three axes. They are transparent and light yellow in colour, and have smooth faces, with good lustre, which give satisfactory reflections. The prism zone contains prominent *a*(100) and *b*(010) faces and occasionally two of the primary prisms *m*(110); but four of these faces on one crystal were not observed. The bipyramid *o*(124) is always well developed, and often the primary brachydomal prism *d*(011) is present as a very small face giving poor reflections. There is a distinct cleavage parallel to *b*(010).

Crystal system: Rhombic normal.

Axial ratios: $a : b : c = 0{\cdot}91900 : 1 : 0{\cdot}82044$.

The table of angles is given below:

Angle.	No. of measurements.	Limits.	Mean.	Calculated.
ab-100 : 010	15	89° 55′— 90° 07′	90° 01′	90° 00′
bm-010 : 110	4	47 09 — 47 18	47 14	47 25
bd-010 : 011	7	50 30 — 50 49	50 39	50 38
oo-124 : $\bar{1}24$	10	56 58 — 57 22	57 12	57 06
oo-124 : $1\bar{2}4$	10	122 40 —122 56	122 46	122 54
oo-124 : $\bar{1}\bar{2}4$	10	49 52 — 50 10	49 58	50 04

The same derivative was also prepared by leaving an equimolecular mixture of *l*- or *dl*-piperitone and anisaldehyde in contact with about three times the weight of concentrated hydrochloric acid for 3 weeks at the ordinary temperature, with occasional shaking. Upon inoculation with crystalline material prepared as above, the gummy product became partly crystalline. The yield of the purified derivative was small, amounting only to about 12% of that recorded above.

Salicylidene-dl-*piperitone*, $C_{10}H_{14}O{:}CH{\cdot}C_6H_4{\cdot}OH$.—The customary method could not be used in this instance, on account of the sparing solubility of the sodium derivative of salicylaldehyde in absolute alcohol. A solution of salicylaldehyde (16 g.) in 10%

aqueous sodium hydroxide was accordingly stirred vigorously with an equimolecular proportion of *dl*-piperitone (20 g.) on a boiling water-bath for 10 hours. The reaction-product was then steam distilled before and after acidification, in order to remove unchanged piperitone (7 g.) and salicylaldehyde, respectively. The residual dark resin when separated and dissolved in hot alcohol yielded successive fractions of crystalline material (8·4 g.); after repeated recrystallisation from the same solvent the product maintained its crystalline characteristics, forming small pale yellow crystals, m. p. 177° (Found: C, 79·6; H, 7·8. $C_{17}H_{20}O_2$ requires C, 79·6; H, 7·9%). Salicylidene-*dl*-piperitone is readily soluble in hot alcohol, and sparingly soluble in cold alcohol, benzene or ether. It forms an orange-yellow solution in sodium hydroxide, but does not dissolve in aqueous sodium bicarbonate.

The same derivative was formed by condensation in presence of concentrated hydrochloric acid, according to the method outlined above for anisylidene-*dl*-piperitone; the yield in this instance was only slightly less than that afforded by the alkaline condensation.

When reduced with zinc dust and alkali, salicylidene-*dl*-piperitone yielded two crystalline products, which appeared to be isomeric dihydro-derivatives having the formula $C_{17}H_{22}O_2$. The first of these, probably formed by normal reduction of the conjugated system in accordance with Thiele's theory, was soluble in aqueous alkali, like the original derivative; it showed evidence of unsaturation, and was not particularly stable. The isomeric reduction product was insoluble in aqueous alkali, and was much more stable than the first product; in this instance the molecule was apparently characterised by the presence of a coumaran ring. These interesting reduction products will form the subject of further study.

Piperonylidene-dl-*piperitone*, $C_{10}H_{14}O{:}CH{\cdot}C_7H_5O_2$.—*dl*-Piperitone (10 g.) and piperonal (10 g., 1 mol.) were dissolved in absolute alcohol (20 c.c.) and mixed with a cold solution of sodium (0·4 g., 0·25 mol.) in absolute alcohol (20 c.c.). Upon keeping the solution at the ordinary temperature crystals soon started to separate, and after 2 days the mixture was poured into water. The crystalline product (16·2 g.) when recrystallised from alcohol melted at 128° (Found: C, 75·8; H, 7·0. $C_{18}H_{20}O_3$ requires C, 76·0; H, 7·1%). Piperonylidene-*dl*-piperitone consists of pale yellow, flaky crystals with a reddish tinge, which persists throughout repeated recrystallisations from alcohol but disappears after recrystallisation from benzene. Apart from this behaviour, no indication of dimorphism was observed. The derivative is readily soluble in benzene or chloroform, and moderately soluble in warm alcohol and ligroin.

Opianylidene-dl-*piperitone*, $C_{10}H_{14}O{:}CH{\cdot}C_6H_2(OMe)_2{\cdot}CO_2H$. — A

solution of sodium (1·9 g.) in absolute alcohol (40 c.c.) was added to a slightly warm solution of *dl*-piperitone (10 g.) and opianic acid (14 g.) in absolute alcohol (40 c.c.). After being kept for 5 days at the ordinary temperature, the mixture was poured into water, the unchanged piperitone being then removed by extraction with ether. When freed from ether and acidified, the clear aqueous solution gave a yellow syrupy precipitate which gradually became crystalline when cooled in ice. Recrystallisation from alcohol furnished pale yellow crystals (8·2 g.), which melted at 157° when heated rapidly. The substance showed no tendency to crystallise in dimorphic forms (Found: C, 69·3; H, 7·2; *M*, by titration, 335. $C_{20}H_{24}O_5$ requires C, 69·7; H, 7·0%; *M*, 344). The derivative is sparingly soluble in hot benzene, but it dissolves readily in chloroform or hot alcohol and also in ammonia or sodium carbonate solutions. It forms insoluble lead, silver, and calcium salts: the *calcium* salt, which is anhydrous, was analysed [Found: Ca, 5·4. $(C_{20}H_{23}O_5)_2Ca$ requires Ca, 5·5%].

Oxidation of Benzylidene-dl-*piperitone*.—To a solution of benzylidene-*dl*-piperitone (8 g.) in acetone (50 c.c.), cooled to 0°, was added with stirring in the course of 3·5 hours a solution of potassium permanganate (20 g.) in a mixture of acetone (400 c.c.) and water (90 c.c.). The resulting precipitate was separated, washed with acetone, dried, and dissolved in a cooled mixture of concentrated sulphuric acid (50 c.c.) and water (350 c.c.). The product obtained from the ether extract of this solution crystallised when kept in a desiccator (2·2 g.). When recrystallised from the minimum quantity of boiling water, it formed colourless crystals, m. p. 94°, and was diagnosed as α-*iso*propylglutaric acid [Found: C, 54·9; H, 7·9; *M*, by titration, 174. $C_6H_{12}(CO_2H)_2$ requires C, 55·2; H, 8·1%; *M*, 174]. The anhydride had m. p. 51—52°, and the anil m. p. 160° (compare Perkin, J., 1896, **69**, 1495). The acetone filtrate in the original oxidation appeared to contain nothing beyond benzaldehyde and some unchanged benzylidene-*dl*-piperitone.

We acknowledge our indebtedness to the McCaughey Research Fund of the University of Sydney for a grant in aid of this work, and we also express our thanks to Mr. W. G. Reid, B.Sc., for carrying out the experimental work on the identification of α-*iso*propylglutaric acid, described above. These investigations are being continued.

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[*Received, April 21st*, 1926.]

CCLXXVIII.—*Preparation of* 3 : 5-*Dihalogenophenols.*

By HERBERT HENRY HODGSON and JOHN SAMUEL WIGNALL.

THE whole series of 3 : 5-dihalogenophenols required in the course of a general investigation of symmetrical substitution in benzene has been prepared from 1 : 3 : 5-trinitrobenzene. Some of them and their derivatives were already known (in most cases the m. p.'s recorded in the literature have been confirmed); the new compounds are described below.

1 : 3 : 5-Trinitrobenzene was prepared by Clark and Hartmann's method ("Organic Syntheses," Vol. II, pp. 93—97), by oxidising 2 : 4 : 6-trinitrotoluene (360 g.) below 45°; a yield of 210 g. was obtained.

5-Nitro-3-aminoanisole was obtained in 85% yield by boiling a mixture of 3 : 5-dinitroanisole (30 g.), sodium trisulphide (18 g.), and alcohol (150 c.c.) for 4 hours, adding water, and extracting the precipitate with boiling dilute hydrochloric acid. It crystallised from water in orange needles, m. p. 120° (Blanksma, *Rec. trav. chim.*, 1905, **24**, 40, gives m. p. 118°; Meister, Lucius, & Brüning, D.R.-P. 22062, give 120°).

The 3-halogeno-5-nitroanisoles were obtained from the preceding compound by the Sandmeyer method, and all crystallised from alcohol in colourless needles. *3-Iodo-5-nitroanisole* has m. p. 84° (Found : I, 45·2. $C_7H_6O_3NI$ requires I, 45·5%).

The 3-halogeno-5-nitrophenols were prepared by heating the 3-halogeno-5-nitroanisoles (10 g.) with concentrated sulphuric acid (30 c.c.) for 2 hours, pouring the mixture on to ice, and crystallising the 3-halogeno-5-nitrophenol from hot dilute mineral acid (yield about 70%). The benzoates crystallise from alcohol, the acetates from water or dilute alcohol, and the 2 : 4 : 6-tribromo-derivatives from dilute acetic acid or alcohol, all in colourless needles. *3-Chloro-5-nitrophenyl benzoate* has m. p. 78° (Found : Cl, 12·6. $C_{13}H_8O_4NCl$ requires Cl, 12·8%), and the *acetate* has m. p. 84° (Found : Cl, 16·3. $C_8H_6O_4NCl$ requires Cl, 16·5%). *3-Bromo-5-nitrophenyl acetate* has m. p. 99° (Found : Br, 30·6. $C_8H_6O_4NBr$ requires Br, 30·8%). *3-Iodo-5-nitrophenol* crystallises from carbon tetrachloride or water in needles, m. p. 136° (Found : I, 47·7. $C_6H_4O_3NI$ requires I, 47·9%), the pale yellow colour of which remains unchanged after repeated crystallisations. The *benzoate* has m. p. 100·5° (Found : I, 34·1. $C_{13}H_8O_4NI$ requires I, 34·4%), and the *acetate*, m. p. 110° (Found : I, 41·1. $C_8H_6O_4NI$ requires I, 41·3%). *2 : 4 : 6-Tribromo-3-iodo-5-nitrophenol* forms colourless plates, m. p. 176°

(0·1337 g. gave 0·2113 g. of mixed silver halides. Required, 0·2127 g.).

3-*Halogeno*-5-*aminoanisoles*.—The chloro- and bromo-compounds were readily prepared by reducing the corresponding nitro-compounds with tin and hydrochloric acid. The following process was more serviceable in the case of 3-iodo-5-aminoanisole: 3-Iodo-5-nitroanisole (12 g.), suspended in a mixture of water (200 c.c.) and concentrated hydrochloric acid (15 c.c.), was heated on the water-bath during the gradual addition of iron filings (24 g.). After 30 minutes, the mixture was rendered alkaline, and the 3-iodo-5-aminoanisole distilled in steam. All three compounds crystallise from light petroleum in colourless needles. 3-*Chloro*-5-*aminoanisole* has m. p. 33° (Found: Cl, 22·5. C_7H_8ONCl requires Cl, 22·5%), 3-*bromo*-5-*aminoanisole*, m. p. 52° (Found: Br, 39·4. C_7H_8ONBr requires 39·6%), and 3-*iodo*-5-*aminoanisole*, m. p. 86·5° (Found: I, 50·7. C_7H_8ONI requires I, 51·0%).

The 3 : 5-*dihalogenoanisoles* were prepared from the 3-halogeno-5-aminoanisoles by the Sandmeyer method. 3-*Chloro*-5-*iodoanisole* is a liquid, b. p. 267—268°, which solidifies at 0° (0·1882 g. gave 0·2672 g. of silver halides. Required, 0·2652 g.). The others all crystallise from light petroleum in colourless aggregates. 3 : 5-*Di-iodoanisole* has m. p. 85° (Found: I, 70·5. $C_7H_6OI_2$ requires I, 70·5%), 3-*chloro*-5-*bromoanisole*, m. p. 33° (0·1026 g. gave 0·1535 g. of silver halides. Required, 0·1534 g.), and 3-*bromo*-5-*iodoanisole*, m. p. 54° (0·1219 g. gave 0·1660 g. of silver halides. Required, 0·1646 g.).

3 : 5-*Dihalogenophenols*.—It was found more convenient to hydrolyse the 3-halogeno-5-aminoanisoles with concentrated sulphuric acid as described above and to apply the Sandmeyer process to the diluted diazotised solution than to replace the amino-group by halogen and hydrolyse the 3 : 5-dihalogenoanisole.

The 3 : 5-dihalogenophenols are moderately easily volatile in steam and crystallise from light petroleum in colourless needles. The benzoates, acetates, and tribromo-derivatives all crystallise from alcohol or dilute alcohol in colourless needles. 3 : 5-*Dichlorophenyl benzoate* has m. p. 55° (Found: Cl, 26·5. $C_{13}H_8O_2Cl_2$ requires Cl, 26·6%), and the *acetate*, m. p. 38° (Found: Cl, 34·3. $C_8H_6O_2Cl_2$ requires Cl, 34·6%).

3 : 5-Dibromophenol has m. p. 81° (Blau, *Monatsh.*, 1886, **7**, 630, gives m. p. 76·5°; Blanksma, *Rec. trav. chim.*, 1892, **12**, 254, gives 81°). The *benzoate* has m. p. 77° (Found: Br, 44·8. $C_{13}H_8O_2Br_2$ requires Br, 44·9%), and the *acetate*, m. p. 53° (Found: Br, 54·5. $C_8H_6O_2Br_2$ requires Br, 54·4%). 3 : 5-*Di-iodophenyl benzoate* has m. p. 93° (Found: I, 56·2. $C_{13}H_8O_2I_2$ requires I,

56·4%). 2 : 4 : 6-*Tribromo*-3 : 5-*di-iodophenol* has m. p. 226—228° (0·1166 g.; 0·2059 g.; 0·2068 g.*).

3-*Chloro*-5-*bromophenol* has m. p. 70° (0·0728 g.; 0·1157 g.; 0·1162 g.), the *benzoate* m. p. 62° (0·1016 g.; 0·1072 g.; 0·1080 g.), and the *acetate* m. p. 45° (0·0716 g.; 0·0911 g.; 0·0950 g.). 3-*Chloro*-2 : 4 : 5 : 6-*tetrabromophenol* has m. p. 205° (0·0657 g.; 0·1312 g.; 0·1323 g.). 3-*Chloro*-5-*iodophenol* has m. p. 60° (0·1273 g.; 0·2385 g.; 0·2393 g.), the *benzoate* m. p. 54° (0·1793 g.; 0·2387 g.; 0·2393 g.), and the *acetate* m. p. 47° (0·1483 g.; 0·2395 g.; 0·2393 g.). 3-*Chloro*-2 : 4 : 6-*tribromo*-5-*iodophenol* has m. p. 195° (0·1229 g.; 0·2350 g.; 0·2356 g.).

3-*Bromo*-5-*iodophenol* has m. p. 82·5° (0·1013 g.; 0·1430 g.; 0·1432 g.), the *benzoate* m. p. 76° (0·1066 g.; 0·1108 g.; 0·1119 g.), and the *acetate* m. p. 46° (0·0723 g.; 0·0884 g.; 0·0896 g.). 2 : 3 : 4 : 6-*Tetrabromo*-5-*iodophenol* has m. p. 220—221° (0·1072 g.; 0·1962 g.; 0·1974 g.).

The authors desire to thank Messrs. J. W. Leitch & Co. and the Nobel Industries Limited for gifts of chemicals used in this investigation.

TECHNICAL COLLEGE, HUDDERSFIELD. [*Received, May 10th*, 1926.]

CCLXXIX.—*The Dependence of Rotatory Power on Chemical Constitution. Part XXIX. The Resolution of Sulphoxides into their Optically Active Forms.*

By PHILIP WILLIAM BENSON HARRISON, JOSEPH KENYON, and HENRY PHILLIPS.

THE preparation of ethyl *p*-toluenesulphinate in an optically active state (Phillips, J., 1925, **127**, 2552) provided substantial experimental evidence that the constitution of this ester was not accurately represented by the usually accepted formula (I).

(I.) $O{=}S{<}^{OEt}_{C_7H_7}$ $\qquad$ $\bar{O}{-}\overset{+}{S}{<}^{OEt}_{C_7H_7}$ (II.)

This formula is also in conflict with the postulates of the newer electronic theories of valency, since the presence of a true double bond between the sulphur and the sulphoxyl oxygen atom would create a surplus of valency electrons (10 instead of 8) in the valency shell of the sulphur atom. According to these theories of valency

* In this and each of the following analyses the three weights recorded are respectively the quantity of substance taken and the quantities of mixed silver halides found and calculated.

the sulphur atom contributes the two electrons that make up the duplet by which its union with the sulphoxyl oxygen atom is denoted, and Lowry has suggested (*Trans. Faraday Soc.*, 1923, **18**, 385) that in such cases the union should be indicated by an electrovalency and a covalency, *i. e.*, by a semipolar double bond. Experimental support for this suggestion has been obtained by Sugden, Reed, and Wilkins (J., 1925, **127**, 1525), who determined the molecular parachors (Sugden, J., 1924, **125**, 1177) of compounds containing sulphur linked to oxygen and deduced that the parachor of this linking (a semipolar double bond) was — 1·6 instead of 23·2 (the parachor of a true double bond). Since the determination of the molecular parachor of ethyl *dl*-*p*-toluenesulphinate (Phillips, *loc. cit.*, p. 2570) revealed that the sulphur and the sulphoxyl oxygen atom were linked by a semipolar double bond, formula (II) was adopted as more accurately representing the constitution of this ester. The newly discovered asymmetric ester molecule could then be considered to assume a tetrahedral configuration in which the apex was occupied by the positively charged sulphur atom, two other corners by the *p*-tolyl and ethoxy-groups respectively, whilst the remaining corner was occupied by the oxygen atom united to the sulphur atom by the semipolar double bond.

From such considerations it was at once evident that an alteration in the accepted formula of sulphoxides (III) could be suggested, and the new formula (IV) carries with it the implication that, like the *n*-alkyl esters of *p*-toluenesulphinic acid, mixed sulphoxides should be capable of existing in an optically active state.

(III.) $O{=}S{<}^{R}_{R'}$ $\qquad\qquad$ $\bar{O}{-}\overset{+}{S}{<}^{R}_{R'}$ (IV.)

4′-*Amino*-4-*methyldiphenyl sulphoxide* (V) and m-*carboxyphenyl methyl sulphoxide* (VI) were therefore prepared and examined, and it was found that they were resolvable into enantiomorphous modifications.

(V.) $\bar{O}{-}\overset{+}{S}{<}^{C_6H_4\cdot NH_2}_{C_6H_4Me}$ $\qquad\qquad$ $\bar{O}{-}\overset{+}{S}{<}^{C_6H_4\cdot CO_2H}_{CH_3}$ (VI.)

Therefore it can now be regarded as definitely established that the fourth valency of quadrivalent sulphur differs from the three other valencies. This experimental fact is in agreement with the electronic theories of valency, according to which sulphur, when quadrivalent, is linked to other atoms by three covalencies and one electrovalency, a conclusion which re-states in other terms the suggestion of Werner (" Lehrbuch der Stereochemie," 1904, p. 317)

that one of the four valency units of quadrivalent sulphur is co-ordinated.

4′-*Amino*-4-*methyldiphenyl Sulphoxide.*

dl-4′-Amino-4-methyldiphenyl sulphoxide (V) was prepared by the interaction of aniline and *p*-toluenesulphinic acid, a method by which Hinsberg (*Ber.*, 1908, **41**, 113), using benzenesulphinic acid and aniline, prepared *dl*-*p*-aminodiphenyl sulphoxide.*

dl-4′-Amino-4-methyldiphenyl sulphoxide readily combined with *d*-camphorsulphonic acid to give a salt which could be recrystallised, without the obvious occurrence of hydrolysis, from water containing a small quantity of that acid. The d-*camphorsulphonate* thus obtained was not optically pure, but nevertheless it gave on decomposition a dextrorotatory *sulphoxide* with $[\alpha]_{5461} + 60{\cdot}1°$ in chloroform solution. This sulphoxide, on repeated recrystallisation from aqueous ethyl alcohol, rapidly reached a constant rotatory power in ethyl-alcoholic solution of $[\alpha]^{25°}_{5461} + 123°$. The lævorotatory sulphoxide recovered from the mother-liquors of the recrystallisations of the *d*-camphorsulphonate was combined with *l*-camphorsulphonic acid. The l-*camphorsulphonate* obtained, after recrystallisation from dilute aqueous solutions of l-camphorsulphonic acid until its rotatory power remained unchanged by further recrystallisation, gave on decomposition l-4′-*amino*-4-*methyldiphenyl sulphoxide* with $[\alpha]^{25°}_{5461} - 122°$ in ethyl alcohol, a value equal in magnitude to that obtained for the dextrorotatory isomeride. Other determinations of the specific rotatory power of the lævorotatory sulphoxide are recorded in Table I.

m-*Carboxyphenyl Methyl Sulphoxide.*

dl-*m*-Carboxyphenyl methyl sulphoxide (VI), m. p. 171—172°, was prepared by the oxidation with hydrogen peroxide of the potassium salt of the corresponding sulphide (Smiles and Stewart, J., 1921, **119**, 1792) dissolved in water. Its *brucine* salt, after

* That during such interactions the R·SO· group enters the aniline nucleus in the *p*-position was proved by Hinsberg (*loc. cit.*), who showed that the aminodiphenyl sulphoxide produced from aniline and benzenesulphinic acid gave an aminodiphenyl sulphide, m. p. 95° (acetyl derivative, m. p. 148°), on reduction. Kehrmann and Bauer (*Ber.*, 1896, **29**, 2364) obtained *p*-aminodiphenyl sulphide, m. p. 93° (acetyl derivative, m. p. 146°), by the following series of reactions, which leave no doubt as to the correct orientation of this sulphide: 4 : 4′-dinitrodiphenyl sulphide, obtained by the interaction of sodium sulphide and *p*-chloronitrobenzene, gave, on reduction with ammonium sulphide, 4-nitro-4′-aminodiphenyl sulphide; elimination of the amino-group from this sulphide and reduction of the *p*-nitrodiphenyl sulphide obtained gave the required *p*-aminodiphenyl sulphide.

TABLE I.

Observed Rotatory Powers of 4'-Amino-4-methyldiphenyl Sulphoxide in Solvents.

c = g. of *l*-sulphoxide in 100 c.c. of solution. $l = 2$. $a = 0{\cdot}02\,c\,[\alpha]$.

		$a_\lambda^{25°}$.			
Solvent.	c.	λ 6708.	λ 5893.	λ 5461.	λ 4359.
Chloroform	1·2580	−1·30°	−1·76°	−2·23°	−4·71°
Ethyl alcohol	1·2110	1·83	2·35	2·95	6·17
Pyridine	1·3375	2·52	3·37	4·21	8·97
1·04*N*-Hydrochloric acid	1·2430	+0·69	+0·86	+1·16	+2·19

recrystallisation from methyl alcohol until no further increase in its rotatory power occurred, gave on decomposition d-m-*carboxyphenyl methyl sulphoxide* with $[\alpha]_{5461} + 125°$ in methyl alcohol. This dextrorotatory sulphoxide was, however, optically impure, since by fractional recrystallisation from mixtures of chloroform and light petroleum it was separated into fractions with slightly different rotatory powers. It was therefore combined with *l*-menthylamine, and the *salt* obtained ($[\alpha]_{5461} + 66°$) recrystallised from acetone until its rotatory power was unaltered by subsequent recrystallisation. It then had $[\alpha]_{5461} + 69°$. On the decomposition of this *l*-menthylamine salt, *d-m*-carboxyphenyl methyl sulphoxide was obtained with m. p. 134°, and with $[\alpha]_{5461} + 137°$ in methyl-alcoholic solution.

The more soluble *brucine* salt recovered from the first mother-liquor was decomposed with *N*-sodium hydroxide solution, a concentrated solution of the sodium salt of the lævorotatory sulphoxide being eventually obtained and acidified. This solution was then extracted with chloroform insufficient in amount to dissolve completely the sulphoxide which had separated. The sulphoxide which remained undissolved had m. p. 170° and $[\alpha]_{5461} - 8°$ in methyl alcohol, whilst the *sulphoxide* recovered from the chloroform extract by the addition of light petroleum had m. p. 133° and $[\alpha]_{5461} - 122°$. Partial solution of the sulphoxide ($[\alpha]_{5461} - 122°$) in chloroform did not lead to any further separation, since the sulphoxide which dissolved was recovered with the same rotatory power. The chloroform did not therefore cause the separation previously observed and it thus appeared that the precipitation of an optically impure sulphoxide from its solution in aqueous sodium hydroxide, by the addition of acids, favoured the formation of the *dl*-sulphoxide, which is sparingly soluble in chloroform. That this explanation is substantially correct was proved by subjecting the sulphoxide with $[\alpha]_{5461} - 122°$ twice to such treat-

ment; it was then recovered from the final chloroform extract with $[\alpha]_{5461}$ — 133·5°. This value (within the limits of experimental error) is almost equal in magnitude to the value obtained for the rotatory power of the dextrorotatory isomeride and it is therefore not surprising that a further repetition of the above process (using the sulphoxide with $[\alpha]_{5461}$ — 133·5°) did not result in any increase in its rotatory power.

Other determinations of the specific rotatory power of the *d*-sulphoxide and of its sodium salt are recorded in Table II.

TABLE II.

Observed Rotatory Powers of d-m-*Carboxyphenyl Methyl Sulphoxide in Solvents.*

c = g. of *d*-sulphoxide in 100 c.c. of solution. $l = 1$. $a = 0{\cdot}01\ c\ [\alpha]$.

		$a_\lambda^{25°}$.			
Solvent.	c.	λ 6708.	λ 5893.	λ 5461.	λ 4359.
Methyl alcohol	2·515	+2·17°	+2·87°	+3·46°	+6·95°
Ethyl alcohol	2·515	2·24	3·09	3·77	7·68
Chloroform *	1·265	2·92	4·07	5·02	10·11
Pyridine	2·515	2·44	3·25	4·04	8·34

* $l = 2$.

The Specific Rotatory Power of the Sodium Salt of d-m-*Carboxyphenyl Methyl Sulphoxide.*

Water †	2·830	+1·70	+2·42	+3·00	+5·98

† This solution was prepared by diluting to the required volume a solution of a known weight of the *d*-sulphoxide in the calculated quantity of standard sodium hydroxide.

Some Properties of the Optically Active Sulphoxides.

Certain notable characteristics of the optically active sulphoxides described are worthy of brief comment. In both the examples studied, the *dl*-sulphoxides are racemic compounds with physical properties widely different from those of the optically active enantiomorphs. For example, when chloroform solutions containing equal quantities of the optically active modifications are mixed, the sparingly soluble *dl*-sulphoxide of much higher melting point crystallises out. This marked racemic character of the *dl*-sulphoxides can be contrasted with the apparently unimolecular character of the liquid ethyl *dl*-*p*-toluenesulphinate as shown by measurements of its surface tension (Phillips, *loc. cit.*, p. 2570).

The asymmetric complex contained in the optically active

sulphoxides is destroyed on oxidation, the sulphones thus produced being optically inactive. In the same way optically active ethyl *p*-toluenesulphinate on oxidation (*loc. cit.*, p. 2579) gave optically inactive ethyl *p*-toluenesulphonate.

It was also shown (*loc. cit.*, p. 2560) that esters of *p*-toluenesulphinic acid which contained the newly discovered asymmetric complex in an optically active state exhibited a marked mutarotation. It was suggested that this might be ascribed to an alteration in the normal linking of the sulphur atom, giving rise to a labile form of these esters which was capable of yielding either stereoisomeride by the reverse isomeric change. An analogous isomeric change has not been detected in the optically active sulphoxides now described; the experiments so far attempted, however, have not been of a sufficiently searching character to reveal a possible slow mutarotation such as was typical of the sulphinic esters. Certain experimental difficulties encountered during the attempts made to find a satisfactory method of decomposing the brucine salt of *d*-*m*-carboxyphenyl methyl sulphoxide without loss of the sulphoxide, suggest, however, that this sulphoxide may readily undergo isomerisation leading to decomposition which may be the counterpart in this compound of the observed mutarotation of the sulphinic esters. In this connexion the study of the dynamic isomerism of benzyl sulphoxide by Smythe (J., 1909, **95**, 349) is of interest, as is also the discovery by Pummerer (*Ber.*, 1909, **42**, 2282) that both *p*-tolyl- and phenyl-sulphoxyacetic acids are readily decomposed by traces of mineral acids into the corresponding aromatic thiols and glyoxylic acid.

Under the experimental conditions employed, *l*-4′-amino-4-methyldiphenyl sulphoxide and its acetyl derivative and also *d*-*m*-carboxyphenyl methyl sulphoxide exhibit complex rotatory dispersion, since curves are obtained when $1/\alpha$ for these compounds is plotted against λ^2. Owing to the relatively complex constitutions of these sulphoxides it is difficult to ascribe this phenomenon to any particular factor. It is possible, however, that it may be connected with their aromatic character * and also with solvent action accentuated by the presence of the semipolar double bond.

Lastly, it is noteworthy that, as in the case of many optically active carbon compounds containing an amino-group, the sign of the rotatory power of *l*-4′-amino-4-methyldiphenyl sulphoxide is reversed in hydrochloric acid solution.

* Optically active secondary alcohols which contain an aromatic nucleus often exhibit complex rotatory dispersion, a phenomenon which is rarely encountered amongst purely aliphatic alcohols (see Part XXV, J., 1925, **127**, 1094).

Experimental.

Preparation and Resolution of dl-4′-*Amino*-4-*methyldiphenyl Sulphoxide.*

dl-4′-*Amino*-4-*methyldiphenyl Sulphoxide.*—A mixture of *p*-toluenesulphinic acid (1 part) and aniline (4 parts) was heated at 110—115° for 30 hours. The excess of aniline was removed in a current of steam, and the non-volatile residue dissolved in ether. The ethereal solution was washed several times with dilute hydrochloric acid, and the *dl*-sulphoxide precipitated from the acid solution by the addition of sodium carbonate. dl-4′-*Amino*-4-*methyldiphenyl sulphoxide* crystallised from ethyl alcohol, after treatment of the hot solution with "norit," in colourless needles, m. p. 169—170°. Yield about 27% (Found: C, 67·6; H, 6·0; N, 6·0. $C_{13}H_{13}ONS$ requires C, 67·5; H, 5·6; N, 6·1%).

On removal of the ether from the washed and dried ethereal solution a non-basic residue remained which slowly crystallised and after crystallisation from ethyl alcohol had m. p. 78°. It was proved to be di-*p*-tolyl disulphoxide by comparison with an authentic specimen prepared from *p*-toluenesulphinic acid by Hilditch's method (J., 1910, **97**, 1096).

Resolution of dl-4′-*Amino*-4-*methyldiphenyl Sulphoxide.*—The *dl*-sulphoxide (55 g.) was dissolved in a hot solution of *d*-camphorsulphonic acid (60 g.) * in water (100 c.c.). The optically impure *d*-4′-amino-4-methyldiphenyl sulphoxide *d*-camphorsulphonate deposited on cooling was recrystallised from water (100 c.c.) containing *d*-camphorsulphonic acid (2 g.).

l-4′-*Amino*-4-*methyldiphenyl sulphoxide.* By the addition of ammonia to the combined mother-liquors from the two crystallisations described above, a lævorotatory sulphoxide (26 g.) was obtained with $[\alpha]_{5461}$ − 37° ($c = 1·0$, $l = 2·0$) in chloroform solution. It crystallised from hot ethyl alcohol on cooling and then weighed 20 g., had m. p. 162—166°, and $[\alpha]_{5461}$ − 24° in chloroform ($c = 1·32$, $l = 2·0$). The more soluble lævorotatory sulphoxide was recovered from the concentrated alcoholic mother-liquor by the addition of water and was obtained as a bulky crop of fine, hair-like needles (6 g.) with $[\alpha]_{5461}$ − 81·5° in chloroform solution ($c = 1·0$, $l = 2·0$). This lævorotatory sulphoxide was dissolved in a hot solution of *l*-camphorsulphonic acid (6·5 g.) in water (25 c.c.), and on cooling, an optically impure *l*-4′-amino-4-methyldiphenylsulphoxide *l*-camphorsulphonate was deposited as rosettes of fine needles. By the addition of water to the filtrate from this

* The theoretical quantity is 55 g. The camphorsulphonates of this sulphoxide were readily hydrolysed, but crystallised uncontaminated by free sulphoxide from dilute aqueous solutions of the camphorsulphonic acids.

salt a lævorotatory sulphoxide was obtained with $[\alpha]_{5461}$ — 10·7° in chloroform solution, showing that the separation was proceeding rapidly. After six recrystallisations from water (containing small quantities of *l*-camphorsulphonic acid) the salt was considered to be optically pure, since the *l*-sulphoxides recovered from a portion of the final crop and from the final mother-liquor had identical specific rotatory powers.

Thus isolated, l-4′-*amino*-4-*methyldiphenyl sulphoxide* l-*camphorsulphonate* had m. p. 133—134°, and $[\alpha]^{25°}_{5461}$ — 18·1° in ethyl-alcoholic solution ($c = 3·75$, $l = 2·0$).

l-4′-*Amino*-4-*methyldiphenyl sulphoxide* obtained by the decomposition of this salt crystallised from aqueous ethyl alcohol in long, slender, hair-like needles, m. p. 151° (Found: C, 67·2; H, 5·9; S, 14·3%). Its specific rotatory powers in various solvents are recorded in Table I.

d-4′-*Amino*-4-*methyldiphenyl sulphoxide*. The optically impure salt of this sulphoxide with *d*-camphorsulphonic acid obtained from the *dl*-sulphoxide as previously described (p. 2085) was recrystallised fifteen times from dilute aqueous solutions of *d*-camphorsulphonic acid. On decomposition of a portion of the final crop a dextrorotatory sulphoxide was obtained with $[\alpha]_{5461}$ + 60° in chloroform ($c = 1·25$, $l = 2·0$), a value identical with the rotatory power of the dextrorotatory sulphoxide obtained from the final mother-liquor. Since five additional crystallisations of the salt produced no further resolution,* it was decomposed and the sulphoxide obtained was twice crystallised from ethyl alcohol. d-4′-*Amino*-4-*methyldiphenyl sulphoxide* was thus obtained, m. p. 151°, with $[\alpha]_{5461}$ + 89·9° in chloroform solution ($c = 1·279$, $l = 2·0$) and $[\alpha]^{25°}_{5461}$ + 123° in ethyl-alcoholic solution ($c = 1·209$, $l = 2·0$), values equal in magnitude, within the limits of experimental error, to those possessed by the *l*-sulphoxide obtained, as described, from *l*-4′-amino-4-methyldiphenyl sulphoxide *l*-camphorsulphonate (Found: C, 67·6; H, 5·8; S, 13·8%).

d-4′-*Amino*-4-*methyldiphenyl sulphoxide* d-*camphorsulphonate* prepared from this sulphoxide had m. p. 133—134° and $[\alpha]^{25°}_{5461}$ + 17·2° in ethyl alcohol ($c = 3·75$, $l = 2·0$).

Recombination of d- *and* l-4′-*Amino*-4-*methyldiphenyl Sulphoxides*. —A solution of the *d*-sulphoxide, m. p. 151° (0·2 g.), in warm ethyl alcohol (1·5 c.c.) was added to a similar solution of the *l*-sulphoxide, m. p. 151°. The needles obtained (0·33 g.) had m. p. 169—170° alone and when mixed with the *dl*-sulphoxide.

* This result was unexpected, since the resolution of an optically impure *l*-4′-amino-4-methyldiphenyl sulphoxide *l*-camphorsulphonate prepared from a lævorotatory sulphoxide with $[\alpha]_{5461}$ −42° proceeded quite normally.

dl-4′-*Acetylamino*-4-*methyldiphenyl Sulphoxide*.—This sulphoxide crystallised from a solution of the *dl*-4′-amino-4-methyldiphenyl sulphoxide (7 g.) in acetic anhydride (7 c.c.). It was obtained after recrystallisation from aqueous ethyl alcohol as bulky, feathery needles, m. p. 183—184° (Found: C, 65·3; H, 5·6. $C_{15}H_{15}ONS$ requires C, 65·9; H, 5·5%).

l-4′-*Acetylamino*-4-*methyldiphenyl Sulphoxide*.—This sulphoxide was prepared as described above from the *l*-sulphoxide and crystallised from aqueous ethyl alcohol in small prisms, m. p. 173—174°. 0·2490 G. was made up to 20 c.c. with ethyl alcohol, and the rotatory power of the solution obtained was determined in a 200 mm. tube at 25°:

	λ 6708.	λ 5893.	λ 5461.	λ 4359.
$\alpha_\lambda^{25°}$	−1·07°	−1·34°	−1·68°	−3·92°
$[\alpha]^{25°}$.....	−43·0	−53·8	−66·2	−157·0

d-4′-*Acetylamino*-4-*methyldiphenyl sulphoxide* prepared from the *d*-sulphoxide was repeatedly crystallised from ethyl alcohol and aqueous acetic acid, but its specific rotatory power in ethyl-alcoholic solution ($c = 1·25$, $l = 2·0$) remained unchanged at $[\alpha]^{25°}_{6708} + 42·0°$, $[\alpha]^{25°}_{5893} + 52·4°$, $[\alpha]^{25°}_{5461} + 66·4°$, values in close agreement with those obtained for the lævorotatory isomeride.

4′-*Acetylamino*-4-*methyldiphenyl Sulphone*.—To a solution of *dl*-4′-amino-4-methyldiphenyl sulphoxide (1·36 g.) in warm acetic acid (50 c.c.), finely ground potassium permanganate (1 g.) was added. The mixture was gently heated and agitated during ½ hour and the solution was then diluted with water and decolorised with sulphur dioxide. The sulphone produced, after recrystallisation from aqueous ethyl alcohol, had m. p. 194° (Found: C, 62·2; H, 5·2. $C_{15}H_{15}O_2NS$ requires C, 62·3; H, 5·2%).

Oxidation of d-4′-*Acetylamino*-4-*methyldiphenyl Sulphoxide*.—1 G. of the *d*-sulphoxide was oxidised as described above. The sulphone obtained had m. p. 192° alone and when mixed with the sulphone obtained by the oxidation of the *dl*-sulphoxide. 0·5 G. made up to 20 c.c. with pyridine was optically inactive to light of λ 5461 and of λ 4359.

Preparation and Resolution of m-*Carboxyphenyl Methyl Sulphoxide*.

m-Chlorosulphonylbenzoic acid (Smiles and Stewart, *loc. cit.*) was reduced in acetic acid solution with zinc and concentrated hydrochloric acid to *m*-thiolbenzoic acid (compare the reduction of *p*-chlorosulphonylbenzoic acid, Smiles and Harrison, J., 1922, **121**, 2024), which was converted into *m*-methylthiolbenzoic acid by treatment of its solution in aqueous sodium hydroxide with methyl sulphate (Smiles and Stewart, *loc. cit.*).

dl-m-*Carboxyphenyl Methyl Sulphoxide.*—The oxidation of *m*-methylthiolbenzoic acid in acetone solution by means of 30% hydrogen peroxide led to the formation of a considerable proportion of *m*-carboxyphenylmethylsulphone (compare Gadzar and Smiles, J., 1908, **93**, 1833). The following procedure was therefore adopted. Hydrogen peroxide (30%; 40 g.) was gradually added with stirring to a solution at 40° of *m*-methylthiolbenzoic acid (30 g.) in water (250 c.c.) containing potassium carbonate (37 g.). The solution obtained was evaporated to a small bulk, cooled, and acidified; impure *m*-carboxyphenyl methyl sulphoxide, m. p. 169—170°, was then precipitated. The crude sulphoxide was dissolved in concentrated hydrochloric acid (4 parts), the insoluble sulphone filtered off, and the filtrate diluted with water; the dl-m-*carboxyphenyl methyl sulphoxide*, m. p. 170—172°, slowly crystallised (Found: C, 51·9; H, 4·5. $C_8H_8O_3S$ requires C, 52·2; H, 4·4%. 0·3182 G. neutralised 0·0685 g. of sodium hydroxide. Theory, 0·0691 g.). *dl-m*-Carboxyphenyl methyl sulphoxide is sparingly soluble in water, ethyl alcohol, benzene, chloroform, and acetone, and it cannot be purified (when contaminated with traces of the corresponding sulphone) by recrystallisation from these solvents.

d-m-*Carboxyphenyl Methyl Sulphoxide.—Brucine salt.* When a filtered solution of brucine (207 g.) and the *dl*-sulphoxide (97 g.) in hot acetone (3 litres) was cooled, the *brucine* salt (245 g.) crystallised; it had m. p. 115° and $[\alpha]_{5461}$ − 13·2° in chloroform ($c = 3{\cdot}95$, $l = 2{\cdot}0$). Since it had $[\alpha]_{5461}$ − 14° after crystallisation from acetone (6 litres), it was crystallised, together with the salt which was recovered from the mother-liquors, from methyl alcohol (500 c.c.). The salt thus obtained (130 g.) had m. p. 128—130° and $[\alpha]_{5461}$ + 8·5° in chloroform ($c = 3{\cdot}96$, $l = 2{\cdot}0$). After twelve further recrystallisations from methyl alcohol subsequent recrystallisation from this solvent and also from water produced no further change in the rotatory power of the salt, which then had m. p. 136—137°, and $[\alpha]_{5461}$ + 40·3° in chloroform ($c = 2{\cdot}00$, $l = 2{\cdot}0$) (Found: C, 64·2; H, 6·2. $C_{31}H_{34}O_7N_2S$ requires C, 64·3; H, 5·9%).

Decomposition of the brucine salt in aqueous solution by an excess or a theoretical quantity of either ammonia, potassium hydroxide, or hydrochloric acid gave much less than the theoretical quantity of dextrorotatory sulphoxide. Titration of aqueous solutions of the salt with *N*/10-sodium hydroxide and phenolphthalein showed that under such conditions the salt was incapable of neutralising the expected quantity of alkali; it was capable of so doing (as a subsequent experiment showed) when dissolved in 50% aqueous ethyl alcohol.

A solution of the final fraction of the brucine salt ($[\alpha]_{5461}$ + 40·3°;

25 g.) in ethyl alcohol (100 c.c.) was therefore diluted with water (55 c.c.), and *N*-sodium hydroxide solution added until the mixture was alkaline. It was then extracted seven times with chloroform to remove the liberated brucine, and the aqueous solution of the sodium salt of the sulphoxide remaining was evaporated to 30 c.c. The ice-cold concentrated solution of this salt was carefully acidified and extracted repeatedly with chloroform. The chloroform extract was dried with anhydrous sodium sulphate and then gave on dilution with light petroleum a crystalline dextrorotatory sulphoxide (6 g.), m. p. 130—131°, $[\alpha]_{5461} + 125°$ in methyl alcohol ($c = 2{\cdot}04$, $l = 2{\cdot}0$). Subsequent crystallisation of this dextrorotatory sulphoxide from mixtures of chloroform and light petroleum indicated that it was not optically pure, since by such means it was divided into fractions with $[\alpha]_{5461} + 128°$ and $[\alpha]_{5461} + 103°$ respectively. The fraction with $[\alpha]_{5461} + 128°$ recrystallised unchanged in rotatory power from chloroform–light petroleum, and in order to test its optical purity its salt with *l*-menthylamine was prepared and recrystallised.

l-*Menthylamine salt.* To a hot solution of the dextrorotatory sulphoxide (4·2 g.; $[\alpha]_{5461} + 128°$) in acetone (30 c.c.) *l*-menthylamine (3·5 g.) in acetone (15 c.c.) was added. On cooling the filtered solution, the l-*menthylamine* salt crystallised; it had $[\alpha]_{5461} + 66{\cdot}4°$ in ethyl alcohol ($c = 2{\cdot}50$, $l = 1{\cdot}0$). After recrystallisation from acetone (500 c.c.) this salt was obtained with m. p. 171° and $[\alpha]_{5461} + 68{\cdot}9°$, a value which remained unchanged after recrystallisation of the salt from acetone. The *l*-menthylamine salt of *d*-*m*-carboxyphenyl methyl sulphoxide thus obtained was dissolved in 50% ethyl alcohol (130 c.c.), and the solution made alkaline with *N*-sodium hydroxide. The liberated *l*-menthylamine was removed by extraction with ether, and the aqueous solution of the sodium salt of the sulphoxide concentrated, cooled, and carefully acidified. The sulphoxide was extracted with chloroform, which was then dried and diluted with light petroleum. The d-m-*carboxyphenyl methyl sulphoxide* thus precipitated (Found: C, 52·2; H, 4·4%) had m. p. 134°, and $[\alpha]_{5461} + 137{\cdot}6°$ in methyl alcohol ($c = 2{\cdot}515$, $l = 1{\cdot}0$). Other determinations of its rotatory power are recorded in Table II.

l-m-*Carboxyphenyl Methyl Sulphoxide.*—A portion of the brucine salt (60 g.) (with approximately $[\alpha]_{5461} - 50°$ in chloroform solution) was dissolved in 50% ethyl alcohol, decomposed by the addition of *N*-sodium hydroxide, and a concentrated solution of the sodium salt of the lævorotatory sulphoxide was obtained from this reaction mixture as previously described. This concentrated solution was then acidified, and the solution and precipitated sulphoxide were

extracted with chloroform. The sulphoxide (5·5 g.) which remained undissolved was removed from the aqueous solution and the chloroform extract. It had m. p. 170—171° and $[\alpha]_{5461}$ — 8·0° in methyl alcohol ($c = 2·5$, $l = 1·0$). From the dried chloroform extract light petroleum precipitated a lævorotatory sulphoxide (10 g.), m. p. 133°, $[\alpha]_{5461}$ — 122° in methyl alcohol ($c = 2·5$, $l = 1·0$). To test whether this sulphoxide could be further resolved by means of chloroform alone, 2 g. were warmed with chloroform (10 c.c.). From the cold chloroform solution, on addition of light petroleum, 0·65 g. of sulphoxide was recovered with $[\alpha]_{5893}$ — 102° in methyl alcohol ($c = 2·52$, $l = 1·0$), whilst the sulphoxide (1·3 g.) which had remained undissolved had $[\alpha]_{5893}$ — 103° under the same experimental conditions. As no separation had occurred, the whole of the lævorotatory sulphoxide ($[\alpha]_{5461}$ — 122°) was dissolved in dilute sodium hydroxide, and the solution obtained acidified and then extracted with chloroform as before. The sulphoxide recovered from this chloroform extract was again submitted to the same process, being finally obtained with $[\alpha]_{5461}$ — 133·5° in methyl alcohol ($c = 2·5$, $l = 1·0$). Repetition of the above process failed to produce any further increase in the rotatory power of this sulphoxide. The *l*-*m*-carboxyphenyl methyl sulphoxide thus obtained had m. p. 133° (Found : C, 52·0; H, 4·4%).

Recombination of the d- *and* l-m-*Carboxyphenyl Methyl Sulphoxides.* —Cold solutions of the *d*- and *l*-sulphoxides in chloroform (0·1 g. in 1·3 c.c.) were mixed. The crystals (0·17 g.), which were precipitated immediately, had m. p. 170°, alone, and when mixed with the *dl*-sulphoxide.

Oxidation of d-m-*Carboxyphenyl Methyl Sulphoxide.* — The *d*-sulphoxide (0·5 g.) in aqueous acetic acid (25 c.c.) was oxidised with potassium permanganate (0·35 g.). Sulphur dioxide was passed through the diluted reaction mixture, from which *m*-carboxyphenylmethylsulphone (0·26 g.) then slowly crystallised in glistening plates, m. p. 230°. 0·201 G. made up to 10 c.c. with 0·1*N*-potassium hydroxide was optically inactive.

Some of the materials used in this investigation were purchased by means of a grant from the Government Grant Committee of the Royal Society and for this the authors wish to express their thanks. One of them (P. W. B. H.) desires to express his indebtedness to the Department of Scientific and Industrial Research for a maintenance grant.

BATTERSEA POLYTECHNIC, S.W. 11. [*Received, April 15th*, 1926.]

The Physical Properties of Glasses. The Relationship to Chemical Composition and Mode of Preparation.

A Lecture delivered before the Chemical Society on April 29th, 1926.

By William Ernest Stephen Turner, O.B.E., D.Sc.

Part I.

Commercial glasses cover a range of compositions comparable in variety with the industrial metallic alloys; and in respect of the number of components present they are usually much more complex than the alloys. The simplest commercial glass is fused silica. Glasses composed of two component oxides have occasional use, such as lead borate and zinc borate, for sealing-in purposes. For the most part, however, the number of major constituents is at least three, and in some cases may be as many as twelve or more.

In practice the glasses are prepared by the high-temperature fusion of the component or components. In the case of silica a temperature of at least 1800° is needed and is obtained electrically. In other cases the fusion of one or more of the acidic oxides, silica, boric oxide, phosphoric oxide, arsenious and arsenic oxides and antimony oxide, with two or more basic oxides, or, more frequently, with metallic salts, is involved. In practice, the oxide itself is employed in the case of lead oxide and, sometimes, of lime. The alkalis are most frequently introduced as carbonates, but also as nitrates, sulphates and borates. The carbonates are more frequently employed than any other salts, this being the usual form in which calcium, barium, magnesium, sodium, potassium and zinc are added.

In discussing the properties of glasses, however, compositions are invariably referred to the proportion of the oxide constituents present. This is the outcome of two causes, the chief of which is the usual method of presenting the results of analysis of a glass; this method in turn is based on the fact that even now our knowledge of the constitution of glasses, and of the particular chemical compounds which are present, is in a very elementary state. In these circumstances it is safer to adopt the plan of describing a glass in terms of its constituent oxides; for example, one containing the elements silicon, sodium and calcium is best described, not as a sodium calcium silicate, but as a soda–lime–silica glass.

As already stated, the number of oxides entering into the composition of a glass may be very considerable. Even in the earliest Egyptian glasses, the composition of which is well authenticated (Table I), namely, those discovered by Flinders Petrie at Tell el

Amarna, as many as thirteen oxides were present in some and eleven or twelve in several of the glasses.

TABLE I.

Composition of Egyptian Glasses from Tell el Amarna * (ca. 1400 *B.C.*).

	Opaque.			Transparent.
	Dark blue.	Leaf-green.	Turkish blue.	Colourless.
SiO_2	61·7	62·44	62·58	63·86
Al_2O_3	2·45	1·00	0·82	0·65
Fe_2O_3	0·72	0·84	0·58	0·67
MnO	0·47	—	—	Trace.
CaO	10·05	9·23	9·33	7·86
MgO	5·14	3·05	4·37	4·18
Na_2O	17·63	18·08	18·19	22·66
K_2O	1·58	2·76	2·75	0·80
CuO	0·32	2·00	0·52	—
Cu_2O	—	—	—	—
PbO	—	0·47	—	—
SnO_2	—	—	0·47	—
SO_3	—	0·72	0·45	—

* Neumann, *Z. angew. Chem.*, 1925, **38**, 776.

No doubt the presence of some of these oxides is more or less accidental, due to the composition of the mineral constituents employed. This applies probably to alumina and lead oxide, but it is quite likely that even at that early date the colouring powers of certain minerals, such as those containing iron oxide, manganese oxide, and the oxides of copper and tin, were understood.

During the next 1400 years, so far as we know, there was no addition of other oxides to the glass-maker's list, although some doubt may be admitted in regard to cobalt oxide. Thompson in his recent "Chemistry of the Ancient Assyrians" refers to the use of arsenic in the glass-making processes of the 7th century B.C.; but I know of no analysis which indicates the presence of such a constituent in any glass of that date. Again, between the first year of the Christian era and 1600 A.D., the only new oxides utilised appear to be those of antimony and phosphorus, but metallic gold was also introduced. Between 1600 and 1800 there were certainly used the oxides of arsenic, lead, boron and cobalt, and of these lead oxide was the most important. In the next 75 years (1800—1875) the list of glass-making constituents tested underwent great expansion. Thus, Fraunhofer introduced bismuth oxide, and Döbereiner strontia and baryta; zinc oxide appears to have been first used by Maes in 1851, whilst Lamy, in 1866, experimented with thallium oxide. Vernon Harcourt's studies (1834—1870) on the effect of chemical composition on the

properties of glass included the oxides of lithium, cadmium magnesium, beryllium, titanium, vanadium, chromium, molybdenum, tungsten, uranium and nickel, and the element fluorine as fluoride. The last fifty years have seen further expansion, and possible constituents now include the oxides of zirconium, germanium, cerium, didymium and other rare-earth elements, as well as the elements carbon, selenium, tellurium, sulphur and chlorine. The work of Schott was largely concerned with bringing to successful commercial application in glasses fluorides and such oxides as alumina, baryta, boric oxide, phosphoric oxide, and zinc oxide.

The study of glasses has therefore come down to the question of the relationship of the effect of the component oxides (or elements) on the physical properties. The list of properties studied is a long one, and includes representatives of the colligative, constitutive, and additive types.

One good instance of a colligative property is the rate of change of mobility in the neighbourhood of the softening temperature. Twyman [1] came to the conclusion that a general relationship existed represented by the equation $M = k \cdot 2^{\theta/8}$. The researches of English [2] on the mobility and viscosity of glass have shown that this relationship holds good for a large number of glasses of differing composition, except for the slight modification that the 8° should be replaced by 9°. In other words the mobility is either doubled or halved according as the temperature rises or falls by each 9°. Gray and Dobbie [3] had previously observed that the specific conductivity of a number of glasses was doubled for each 9° rise in temperature.

The constitutive properties include the viscosity, the annealing temperature (which depends directly on the viscosity), light absorption and transmission, both general and selective, the electrical conductivity, and—what is to be regarded partly as a chemical process, since it usually involves hydration and hydrolysis—the resistance of glass to the action of water, aqueous solutions, acid solutions, and the alkalis. It is necessary in a lecture of limited scope to make a choice of subjects, and the plan which I decided to adopt was to discuss those properties of glass which have been the subject of investigations during the past few years and are more or less directly of interest to the chemist.

In connexion with the subject of light transmission and absorption I will content myself with reference to a number of problems of a definitely chemical character which still await solution. It is known, for example, that slightly tarnished camera lenses, owing to the reduction of the amount of light lost by reflection, are " faster " than when the surface is freshly polished. Wright and Ferguson [4] have confirmed this fact and found that suitable modification of the surface

can be brought about by the action of solutions of many salts, but in different degrees. Sodium dihydrogen phosphate in 1% aqueous solution acting for 18 hours at 80° is one of the most successful. A satisfactory theory of the action is yet wanting. The study of the changes in colour associated with the process of decolorising glass presents another very interesting field awaiting more thorough cultivation. A small fraction of 1% of iron oxide in the ferrous condition imparts a greenish tint to glass, sufficient to be detected in a thickness of about 2 cm. when as little as 0·02% is present. For use in table glassware and general domestic purposes, this tint is corrected (decolorised) partly by the use of oxidising agents, such as nitrates, to convert the green lower oxide into the straw-coloured ferric condition, and partly by the addition of some constituent, such as manganese dioxide, nickel oxide or selenium, which provides a tint complementary to that due to the iron oxide present. The decolorised state is not permanent and colour changes may subsequently occur which indicate the occurrence of slow chemical changes involving oxidation and reduction in a medium so immobile as glass. Thus, exposure to strong sunlight gradually turns purple those glasses decolorised at an earlier stage by manganese dioxide, whilst glasses decolorised by selenium or by arsenious oxide —itself a decolorising agent of not definitely-known function—turn yellow. Even the bright greenish tint in glass to which no decolorising agent has been added turns yellowish-green on long exposure to light and it may be remarked that soda glasses are more difficult to decolorise than those containing potash, probably because of the greater viscosity of potash glasses as the result of which the dissociation of ferric into ferrous oxide with liberation of oxygen is retarded.[5]

The other four properties mentioned have certain aspects in common, but it will be of interest to refer to each separately before indicating their inter-relationships.

The viscosity of glass is a property of the greatest importance to the glass-maker. Until quite recently the attempts to determine the viscosity of glass had been few and unsystematic, but in the last three years three groups of investigations have widely extended our information on this subject: Washburn, Shelton and Libman [6] in America, Stott,[7] and Stott, Irvine and D. Turner,[8] at the National Physical Laboratory, and English [9] at Sheffield, have been responsible for these investigations. All the investigators have covered somewhat similar ground, but as the work of English deals with a greater range of oxides it will be made the basis of a few remarks on this subject.

The range of variation of viscosity varies greatly between the

temperature at which the glass is present in the furnace and that at which it becomes too stiff for manipulation. Thus, a glass containing 75% SiO_2, 16% Na_2O, 8·16% CaO, which is typical of much commercial soda–lime–silica glass, has a viscosity at 1392° of $1{\cdot}54 \times 10^2$ *C.G.S.* units, whilst at 726° it is $4{\cdot}3 \times 10^7$, a difference of more than 200,000 times. At a temperature which is suitable for the annealing of this glass, namely, 550°, the viscosity is in the neighbourhood of 10^{13} *C.G.S.* units. By the study of a series of glasses in which silica and soda were constituents, and in which the third constituent was lime, magnesia, alumina or boric oxide, it has been found that the viscosity of the glass increases in the order lime, magnesia, alumina. Glasses containing boric oxide are comparatively fluid. The rate of change of viscosity, however, takes place in the inverse order, the alumina-containing glasses setting most slowly and the lime-containing most quickly when comparing the three oxides. The fluid boric oxide-containing glasses likewise set with increasing rapidity as the boric oxide content is increased.

The viscosity of glass controls the rate of diffusion and also the ease with which the glass can be manipulated and worked into objects. The high viscosity accounts for the slow rate of diffusion and for the existence of inhomogeneities such as are seen in their gross form as cords and waves, and in their finer form as striæ. The former marred a good deal of the earliest chemical ware produced in this country. Most of the glasses prepared for this purpose contained between 5 and 10% of alumina, as well as other oxides such as that of zinc, which produce glasses of high viscosity. Mechanical stirring is essential in order to promote homogeneity when the glass is prepared for optical purposes. If the inhomogeneity revealed in waves, cords, and stripes is considerable, then, because each portion has its own viscosity and rate of setting, as well as its corresponding thermal expansion and mechanical properties, stresses are set up which cannot be removed by the annealing process, whilst if the article passes successfully through the annealing furnace it will often fracture spontaneously shortly afterwards.

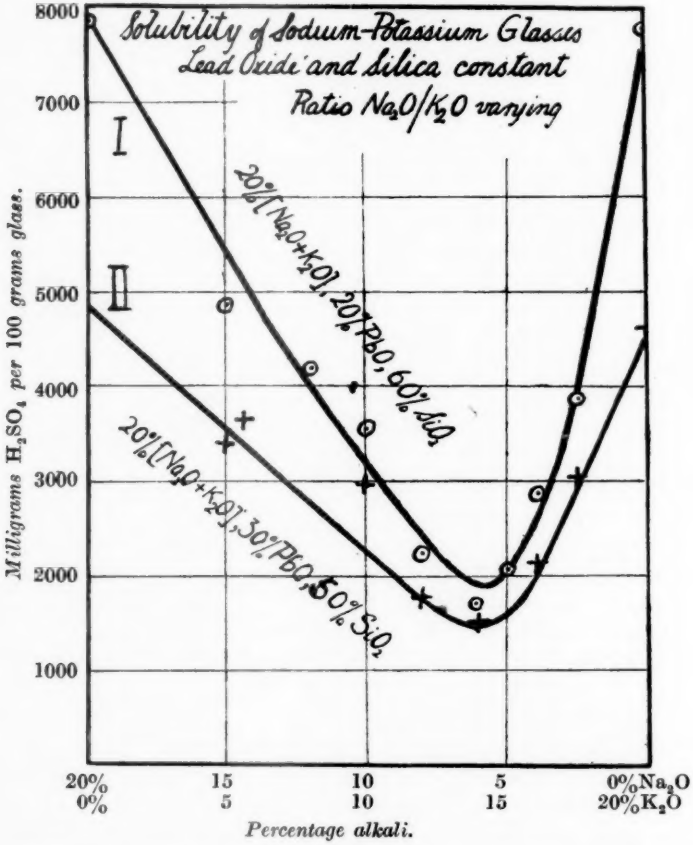
The annealing temperature is directly connected with the viscosity, since removal of stresses can only take place when the glass possesses sufficient mobility. English and Turner [10] and Sheen and Turner [11] have published the results of annealing temperature measurements as related to the composition of glass containing the oxides SiO_2, Na_2O, CaO, MgO, Al_2O_3, B_2O_3, TiO_2, ZnO, BaO, ZrO_2, and English has subsequently shown that the determined annealing temperatures actually correspond to the temperature at which the logarithm of the viscosity of the glass is approximately 12·75.

The electrical conductivity of glass within the range in which it

is still rigid has been the subject of recent investigations by Ambronn [12] and still more recently by Gehlhoff and Thomas.[13] The electrical conductivity of glass is electrolytic in character and the form of the curves showing the relationship between electrical conductivity and temperature for similar series of glasses bears a

FIG. 1.

Alkali extracted by water at 80° from finely powdered soda-potash-lead oxide-silica glasses.
(C. J. Peddle.)

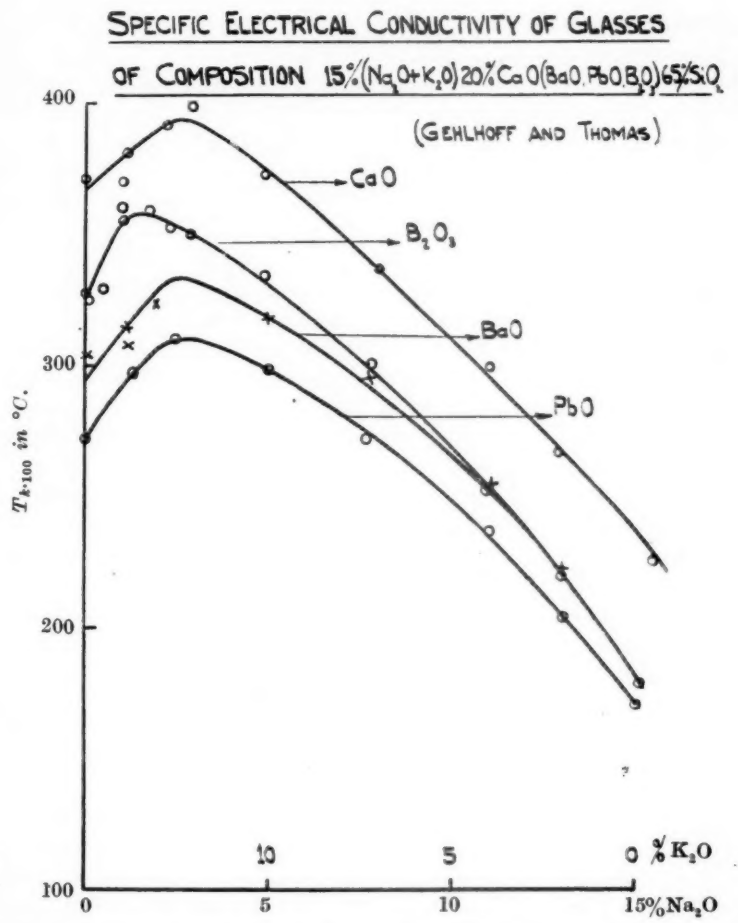


distinct resemblance to the mobility curves. The governing factor in the conductivity of glass, especially at the lower temperatures, thus appears to be the viscosity of the medium.

It was pointed out by Kohlrausch that the insulating properties of a glass were dependent on its power of resisting the action of water—in other words, on its chemical durability. This relationship

was strikingly confirmed by Gehlhoff and Thomas in connexion with glasses containing both soda and potash as alkaline constituents. It had previously been shown by Peddle [14] that, in alkali–lead oxide–silica glasses containing both soda and potash, the maximum resistance to the attack by water was reached when the ratio of the

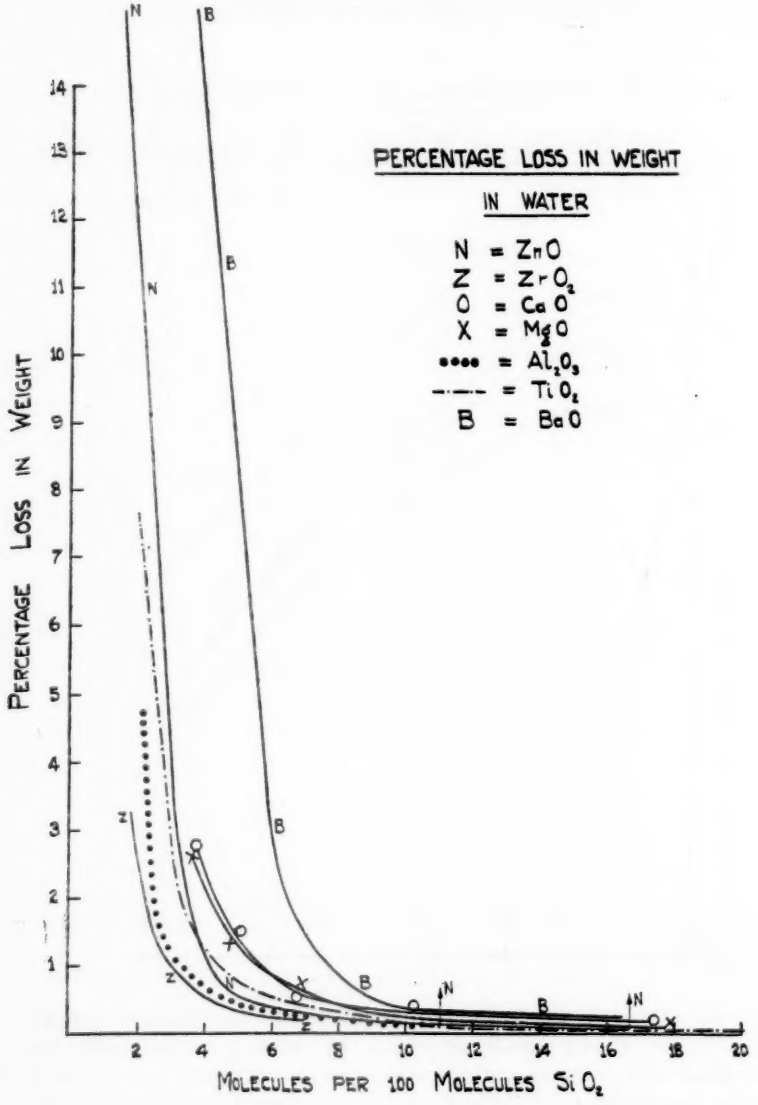
FIG. 2.



potash to the soda was in the proportion of 7 to 3, in parts by weight (Fig. 1), and that generally speaking the resistance was greater for the glass containing the mixed alkalis than when only one of these oxides was present. Gehlhoff and Thomas found a similar relationship in that the specific resistance also reached a maximum corresponding to the maximum resistance to the attack by water.

This fact the authors set out graphically (Fig. 2) by plotting against the percentages of soda and potash the value of the

FIG. 3.



temperature (T_{k100}) at which each glass had the same electrical conductivity, *viz.*, 100×10^{-10} mho per cm. The higher the

temperature the greater must be the electrical resistance of the glass.

The resistance of glass to water and chemical reagents is of first-class importance to the chemist. A very great deal of work on this subject has been carried out at Sheffield, and the results may be set out very briefly. Comparison of the durability of glasses has been made in various ways, but one of them has been exploited by us fairly fully. In this particular series of investigations (not hitherto published), a parent glass corresponding to the approximate formula $6SiO_2,2Na_2O$ was prepared, and for the soda were substituted, stage by stage, lime, magnesia, alumina, titania, zirconia, zinc oxide, and barium oxide, providing for test some sixty glasses in this series alone. The effect of boric oxide will be referred to at a later stage.

In Fig. 3 the resistant power, determined by the percentage loss in weight sustained on boiling in water for 1 hour a fixed weight of the glass in the form of powder of definite grain size, is set out to show the variation with chemical composition. The comparison is made on the basis of molecular composition. It will be seen that in each case replacement of the sodium oxide by a small amount of one of the other oxides mentioned results in a rapid increase of resistant power. The resistance, as shown by the curves, appears to increase in the order barium oxide, lime, magnesia, titania, zinc oxide, alumina and zirconia. If we bear in mind that the glasses rich in the alkali oxides soda and potash are very readily attacked by water, and that the glasses rich in silica are highly resistant, we shall see that a very rough and ready rule exists, namely, that the glass is all the more resistant as the soda is replaced progressively by an oxide of very low solubility in water; thus barium oxide, calcium oxide and magnesia have a distinct solubility in water, diminishing in the order stated, whilst at the other end alumina, zirconia and silica are practically insoluble.

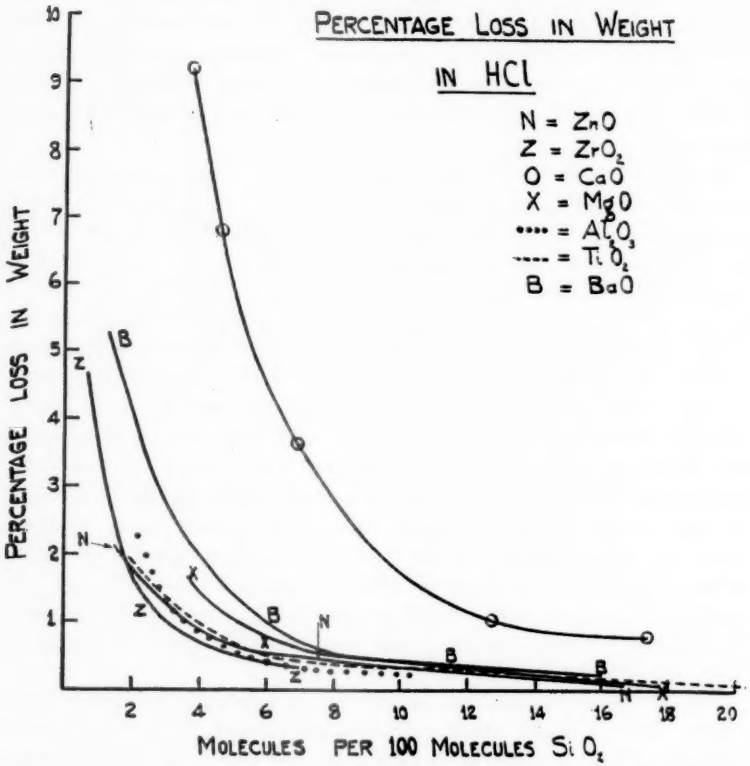
The action of neutral salt solutions is, generally speaking, practically that of water itself. The same remark holds good for a number of dilute acids such as nitric and sulphuric, and concentrated sulphuric acid has been found in some cases to have a smaller corrosive action than pure water. Hydrofluoric acid reacts with silicate glasses, as also does phosphoric oxide above 400°. Of the commonly used acids, hydrochloric acid apparently provides the most searching test of a glass in regard to resistance to acids. For test purposes at Sheffield we have selected hydrochloric acid of 20·24% strength as a standard reagent. Fig. 4 shows the relative resistance of the glasses to this acid.

In the case of alkaline solutions, whether those of alkaline salts

or of caustic alkali, the corrosion is usually very much greater than is caused by water or acids. This is not unexpected in view of the fact that most commercial glasses contain 70% of silica or other acidic oxides.

The third group of properties is that in which additive relationships exist. The first of the properties for which Winkelmann and Schott found this type of relationship is thermal expansion, and the result

FIG. 4.



of studies at Jena of other physical properties of glasses disclosed a number of similar character. The equation which is made to fit the results in all cases contains the same number of terms as the number of oxides present in the glass. Thus, the cubical thermal expansion coefficient of glass can be calculated by the equation devised by Winkelmann and Schott, namely, $3\alpha = ap_1 + bp_2 + cp_3 + \ldots$, in which p_1, p_2, p_3, etc., represent the percentages by weight of the various constituent oxides in the glass, and a, b, c, etc., are constants depending on the nature of the oxide. The constant

in question is the contribution which each 1% of the constituent oxide makes to the total cubical expansion of the glass.

A similar linear relationship exists for the specific volume, and the density may be calculated from the formula $100/D = p_1/d_1 + p_2/d_2 + p_3/d_3 +$ etc., in which D represents the density of the glass, p_1, p_2, p_3, etc., the percentage of each oxide, and d_1, d_2, d_3, etc., the constants for the individual oxides.

Like formulæ have been derived to express the data obtained in the case of the thermal conductivity, the tensile strength, the compressibility, specific heat, Young's modulus of elasticity, and hardness.

On some of these properties very little systematic work has been carried out since that of Winkelmann and Schott, and further reference will be confined to the thermal expansion, density and refractive index which have been the subject of many recent investigations. It may, however, be mentioned in passing that two recent investigations on glasses and silicate rocks, namely, one by Adams and Williamson [15] and the other by Bridgman,[16] have shown the general additive character of the relation between compression strength and composition.

The thermal expansion, which is an important element in the thermal endurance of chemical and heat-resisting glass, has been the subject of systematic investigation at Sheffield. Winkelmann and Schott's work was based on glasses of very varying composition. At Sheffield we have studied series of glasses of similar molecular composition, namely, those based on the formula $6SiO_2,(2-x)Na_2O,xRO$ (R_2O_3 or RO_2), and the results, summarised in Fig. 5, for glasses containing lime, magnesia, alumina, zinc oxide, barium oxide and zirconia indicate the existence of a definite linear relationship over a considerable range of composition as sodium oxide in the parent glass is replaced step by step by one of the oxides mentioned. We have found that a number of Winkelmann and Schott's constants are in error: that for silica, for example, appeared to be distinctly high. The basis of the calculation by these two workers was empirical. We have set out on the assumption that in the above glasses silica exercises its own thermal expansion, and the comparative values ($\times 10^9$) are summarised in Table II, those of Winkelmann and Schott being denoted by W. & S. and those of English and Turner by E.& T. The value for ZnO must be regarded as provisional.

TABLE II.

Constants for Calculating Cubical Thermal Expansion.

	SiO_2.	Na_2O.	CaO.	MgO.	ZnO.	Al_2O_3.	ZrO_2.
W. & S.....	80	1000	500	100	180	500	—
E. & T.	16	1300	490	135	(20)	40	70

Fig. 5.

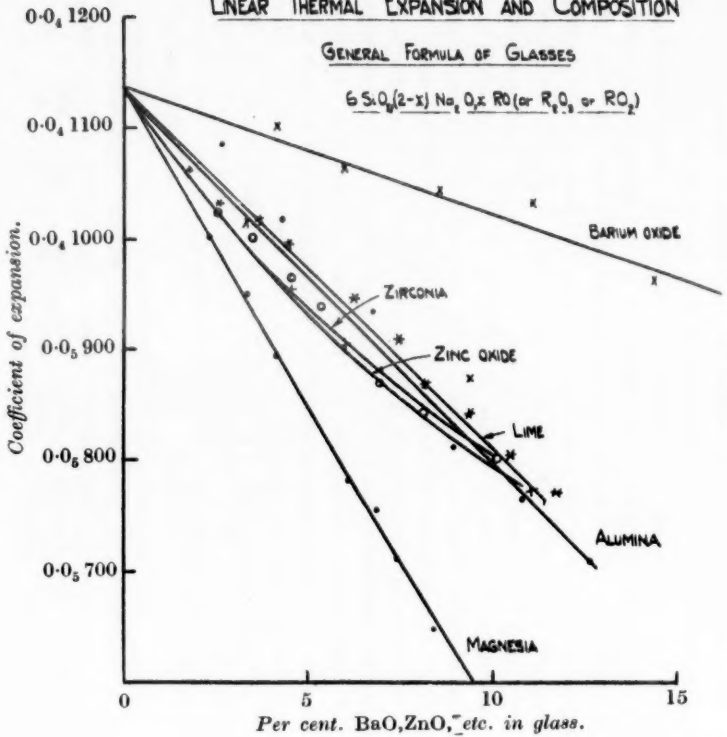
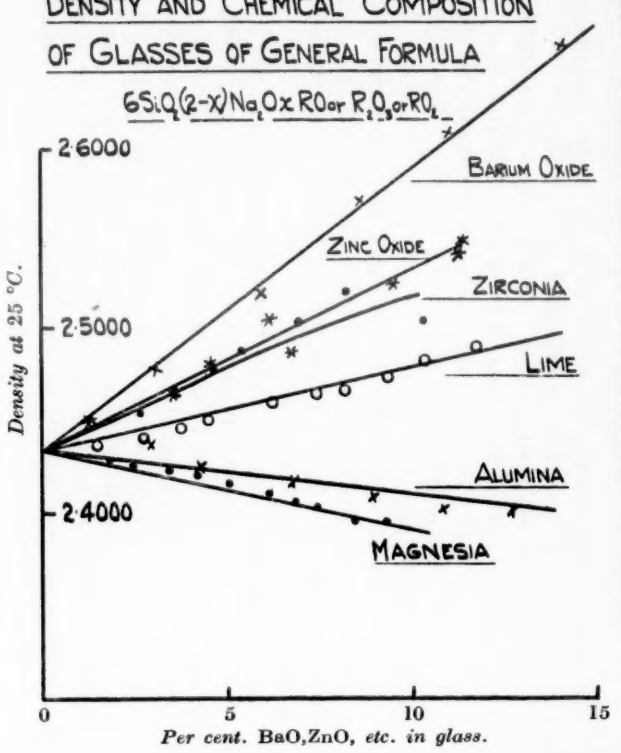

LINEAR THERMAL EXPANSION AND COMPOSITION
GENERAL FORMULA OF GLASSES
$6SiO_2(2-x)Na_2O x RO$ (or R_2O_3 or RO_2)
$0{\cdot}0_4$ 1200
$0{\cdot}0_4$ 1100
$0{\cdot}0_4$ 1000
$0{\cdot}0_5$ 900
$0{\cdot}0_5$ 800
$0{\cdot}0_5$ 700
Coefficient of expansion.
BARIUM OXIDE
ZIRCONIA
ZINC OXIDE
LIME
ALUMINA
MAGNESIA
0
5
10
15
Per cent. BaO, ZnO, etc. in glass.

Fig. 6.


DENSITY AND CHEMICAL COMPOSITION
OF GLASSES OF GENERAL FORMULA
$6SiO_2(2-x)Na_2Ox RO$ or R_2O_3 or RO_2
2·6000
2·5000
2·4000
Density at 25 °C.
BARIUM OXIDE
ZINC OXIDE
ZIRCONIA
LIME
ALUMINA
MAGNESIA
0
5
10
15
Per cent. BaO, ZnO, etc. in glass.

Saltpeter,[17] referring to Winkelmann and Schott's constants, pointed out that the oxides of high value, like soda and potash, contain elements which occupy peaks on the atomic volume curves, whilst those of low value contain elements which occupy the depressions. On this basis, some of the constants, such as those of zinc oxide and alumina, needed revision. Our own constants are more in keeping with the generalisation.

The relationship between density and composition has also been investigated at Sheffield and the results are summarised in Fig. 6. Again the general linear relationship holds good. Constants are likewise available for the calculation of density. We have not yet provided a completely revised set but those worked out by Baillie [18] can be used satisfactorily for the purpose of approximate density calculations.

The refractive index and dispersion are also largely additive in character. This appears to be the case for glasses of the general series $6SiO_2,(2-x)Na_2O,xRO$ (see, for example, Clarke and Turner,[19] for the soda–lime–silica glasses). Peddle has made comprehensive measurements of the relationship between refractive index and composition and the additive character revealed may be illustrated by reference to Fig. 7 for potash–lime–silica glasses.

The simplicity of these relationships in practice, whatever they mean in theory, makes it possible to prepare glasses of approximately known properties by bringing together suitable oxides in the requisite proportions. For example, the preparation of optical glasses of specified refractive index is rendered easier by the general additive relationships subsisting. The development of heat-resisting glasses in practice has largely resulted from a study of the thermal expansion constants combined with improvement in the melting capacity of furnaces so as to make it possible to use as components of the glasses those oxides of high melting point, particularly silica, which contribute only slightly to the total thermal expansion. In this connexion the alkaline oxides soda and potash are to be avoided wherever possible. They are the controlling factors in the thermal expansion as well as in the action of water and chemical agents on glasses containing them. The special virtue of these oxides lies in the greater ease of melting which they impart to glasses; but so far as chemical durability and physical properties are concerned their influence is generally detrimental.

The bearing of the facts which have been related on chemical resistance glass can be very well illustrated by reference to Table III containing the compositions determined by analysis, of the latest types of chemical resistance glasses available. The analyses are our own where no other source of information is quoted.

FIG. 7.

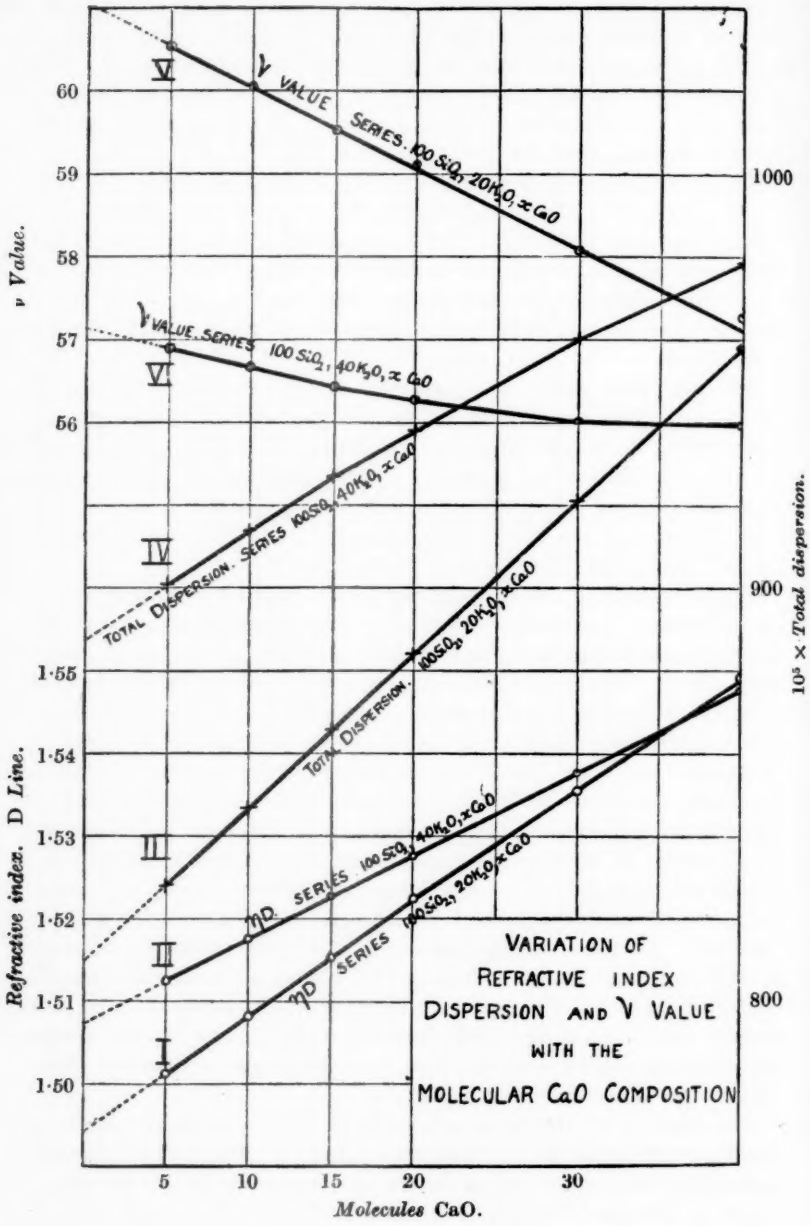

ν Value.
Refractive index. D Line.
10³ × Total dispersion.
Molecules CaO.
ν VALUE SERIES. 100 SiO₂, 20K₂O, x CaO
ν VALUE SERIES 100 SiO₂, 40K₂O, x CaO
TOTAL DISPERSION. SERIES 100SiO₂, 40K₂O, x CaO
TOTAL DISPERSION. 100SiO₂, 20K₂O, x CaO
ηD SERIES 100 SiO₂, 40K₂O, x CaO
ηD SERIES 100 SiO₂, 20K₂O, x CaO
VARIATION OF REFRACTIVE INDEX DISPERSION AND ν VALUE WITH THE MOLECULAR CaO COMPOSITION
V
VI
IV
III
II
I

TABLE III.

Chemical Composition of Some Modern Resistant Glasses.

	SiO_2.	B_2O_3.	As_2O_3.	Sb_2O_3.	Al_2O_3.	Fe_2O_3.	CaO.	MgO.	ZnO.	BaO.	K_2O.	Na_2O.
Chance Bros.* (1924)	71·2	12·0	—	3·4	3·5	0·1	1·3	—	—	—	—	8·6
Duroglass (1916)...	66·5	1·6	—	—	6·7	0·1	4·3	0·3	3·6	—	2·6	11·5
Durosil (1925)	72·3	12·6	—	—	4·2	0·1	0·5	0·1	3·3	—	1·4	5·0
Jena † (1920)	74·5	4·6	—	—	8·5	—	0·8	0·1	—	3·9	—	7·7
Moncrieff (1916) ...	66·4	6·9	—	—	6·6	0·1	0·5	0·1	8·7	—	1·1	10·0
Moncrieff-Monax * (1926)	75·3	11·3	—	—	3·0	—	0·5	—	2·8	—	1·2	6·3
Pyrex (1917)	80·6	11·9	0·7	—	2·0	0·1	0·2	0·2	—	—	0·6	3·8
Resista ‡ (1923) ...	81·4	10·6	—	—	2·0	—	0·7	—	—	—	1·1	4·4
Resista ‡ (1925) ...	75·3	15·8	—	1·3	2·5	—	—	—	—	—	1·0	3·4
Sv Resistance (1925)	81·3	10·1	—	—	3·9	0·1	—	—	—	—	0·4	4·2
Wood Bros.* (1926)	59·3	9·6	—	—	7·6	—	5·0	1·7	5·2	—	2·9	8·8

* Private communications.
† Keppeler, *Z. Verein. deutsch. Ing.*, 1923, **26**, 509.
‡ Thiene, *Glas u. Apparat*, 1924, **5**, 1; *Z. angew. Chem.*, 1926, **39**, 193.

It will be noticed from this table that the silica content with three exceptions exceeds 70% and the total of the acidic oxides, mainly silica and boric oxide, generally runs high. The Jena glass of 1911 and the glasses of the war-time period, both in this country and in America, in most cases had a silica content between 64·5 and 68%. The total proportion of basic oxides, except in the case of Pyrex glass, was accordingly distinctly higher. As glass for chemical purposes may have to withstand the action of water and of acids and alkalis, some sort of compromise has to be effected for the simple reason that a glass may be expected to be all the more readily attacked by alkalis the richer it is in acid oxide constituents. In the last few years, the tendency has been to sacrifice something of the resistance towards alkaline solutions and to concentrate on improving the resistance towards water and acid solutions. Silica is eminently suitable for this purpose, and in the case of the action of water, the presence of boric oxide within certain limits is also advantageous. Hence, the most recent glasses contain silica, boric oxide, and alumina as three of the chief components, and only such proportions of alkaline and other oxides as may be desirable to produce fairly ready melting. It will be noticed how closely a number of recent glasses are attempts to copy Pyrex glass, which was brought out in 1915.

Whilst sacrificing a little of the resistance towards alkaline reagents, the use of a high percentage of silica, and, within limits, of boric oxide, reduces substantially the thermal expansion of the glass and renders it increasingly immune from sudden changes of temperature. In fact, the glasses which most readily furnish resistance to the action of water and acids are also those which are the best heat-resisting glasses.

Part II.

Up to this stage our account of the properties of glass has been descriptive and on the whole the impression probably given is that of comparatively simple relationships. Even in properties described as constitutive the mass factor operates; that is to say, there is a more or less continuous variation in the viscosity or electrical conductivity or resistance to chemical reagents as the proportion of a specific oxide in the glass is increased. The existence of so many additive relationships suggests a comparatively simple constitution for glasses. There are some workers, indeed, for example, Sosman [20] and Tammann,[21] who suggest that in glasses the oxides are in a state of dissociation. This presents possibly no greater anomaly than the case of aqueous or other solutions. The suggestion of Sosman is that possibly compounds are only definitely established at the moment of their separation in the form of crystals from the glass. The specific-volume curve for mixtures of magnesium and calcium silicate shows a definite break for the crystalline mixtures, but not for the glasses containing the same components in the same proportions. Definite evidence of the existence of compounds in glasses has yet generally to be established. In the simple system sodium oxide–silica, when the specific volume and also the specific refraction are plotted against the composition, a definite break occurs in each case at a point corresponding to $Na_2O,2SiO_2$.[22] This particular compound was first isolated from melts and characterised by Morey and Bowen [23] only in 1924. The systematic investigation of the constitution of glasses through a study of the variation of physical properties is only just being taken up.

A large number of silicates have been isolated from silicate fusions containing the oxides employed in making commercial glasses. Thus, by suitable thermal treatment of fusions of soda–lime–silica, deposition has been obtained not only of the simple silicates Na_2O,SiO_2; $Na_2O,2SiO_2$; CaO,SiO_2; and $2CaO,SiO_2$, but also of a series of complex compounds, namely, $2Na_2O,CaO,3SiO_2$; $Na_2O,2CaO,3SiO_2$; and $Na_2O,3CaO,6SiO_2$, each characterised by extensive dissociation when liquefied.[24]

The examination of glasses by *X*-rays has not yet revealed any marked structure, although Wyckoff and Morey in 1925, in a study of the *X*-ray diffraction patterns of the soda–lime–silica glasses, found both broad bands and in some cases lines, the precise interpretation of which has yet to be made.

If we bear in mind the number of the components which Morey and Bowen have already shown to be capable of existence in the system soda-lime–silica, and if, further, we assume that some or all

of them exist in the glass, we shall be better able to appreciate the possibility of some of the anomalous results which will presently be referred to as having in very recent years been observed to exist in certain properties of glasses.

Before passing on to this subject, however, and while the subject of the constitution of glass is being considered, reference may be made to the similarity in the behaviour of certain glasses to zeolites such as heulandite and desmine. These zeolites are characterised by their power of parting with a considerable proportion of their water without loss of structure or optical properties. Moreover, it is possible by means of concentrated hydrochloric acid to withdraw the whole of the basic constituents, leaving the residual silica as a skeleton in which the original structure is preserved. It is a striking fact that samples of ancient glass, on treatment with hydrochloric acid, frequently behave in a very similar way, the basic constituents being withdrawn and a silica skeleton remaining. This, however, is true not only of ancient glass, but also of certain newly melted glasses which are readily attacked by water and by hydrochloric acid. Thus, we have found it possible in the case of a sample of glass tubing of percentage composition, SiO_2 49·5, B_2O_3 25·7, CaO 9·08, Na_2O 7·0, and K_2O 7·5, to extract by means of hot hydrochloric acid of strength not less than 20·24% all other constituents from the glass except the silica, the latter retaining the form of the original tube.[25] The silica at no stage appears to exist in the gelatinous form. Whatever bearing this may have on the constitution of glass, it is at least a reasonable surmise that the zeolites were probably glasses which through weathering action have been so modified as to render their constituents easily capable of extraction or substitution, the silica in the meantime having slowly developed a lattice accompanied by definite optical properties and crystalline form.

I now wish briefly to direct attention to three factors influencing the properties of glass, namely, the influence of concentration and specific composition, the effect of the mode of preparation, and finally the influence of heat treatment.

1. *The Effect of Concentration and of Specific Oxides.*

In the case of the basic constituents of glass, as also of silica in silicate glasses, our present information shows that there is continuous variation of the physical property directly with the variation of composition and frequently in an additive manner. For the system of glasses Na_2O–SiO_2, the curve showing the variation of thermal expansion with composition is nearly straight over a considerable range, so straight over such a length as to suggest that silica in these

glasses exercises the thermal expansion it possesses in the free vitreous state.[26] The refractive index and density curves for mixtures of albite and anorthite, as well as for magnesium silicate and calcium silicate, over the whole range from 0 to 100% of each are either rectilinear or nearly so.[27]

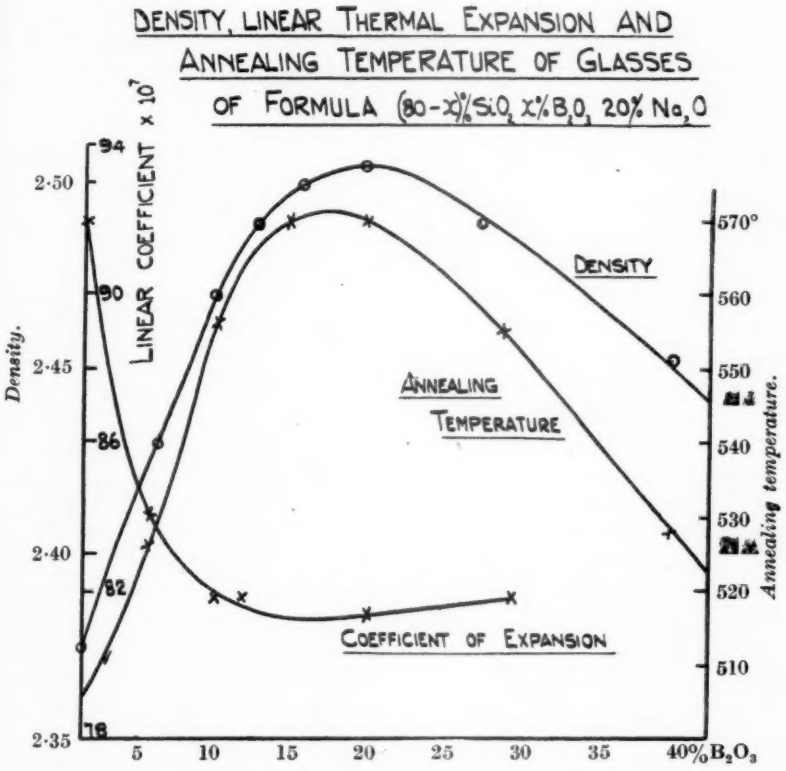
In some series of glasses the graphs show a marked tendency to be concave or convex to either axis. Instances occur in the thermal expansion curve for titania-containing glasses [28] and in the refractive index curves of some series examined by Peddle.

Finally, the occurrence of inversion points has already been referred to in the physical properties of glasses containing mixtures of sodium oxide and potassium oxide. Thus, the resistance to the action of water attains a maximum at a certain ratio of potash to soda, namely, 7 : 3, whilst the specific resistance similarly reaches a corresponding maximum. It is also of interest to note that the after-contraction which takes place in glass, especially as revealed in thermometer bulbs, is greatest when both alkaline oxides are present and the after-contraction can only be made more or less negligible by using a glass containing one alkali oxide only. The precise ratio of soda to potash which gives the maximum after-contraction has not been generally determined. It may prove to coincide with the maxima on the water-resistance and the electrical-resistance curves.

Boric oxide is another constituent which does not follow additive relationships over a wide range of concentration. Great value has been attached to this oxide as a constituent for chemical and heat-resisting glass and almost all modern glasses of these types contain it. During lengthy investigations at Sheffield 8 to 9 years ago on the subject of chemical glassware we came to the conclusion that it was a constituent of limited usefulness and especially in the case of glasses intended to resist hydrochloric acid. Further researches between 1923 and 1925 showed that this limit definitely exists. Fig. 8 shows the influence of boric oxide on the density, the annealing temperature, and thermal expansion of glasses of the system soda–boric oxide–silica in which the sodium oxide content is approximately 20% throughout the series. It will be seen that a minimum occurs in the thermal expansion curve and maxima in the other two cases. Moreover, a maximum occurs in the resistance to the action of water, after which the glass breaks down rapidly. In Fig. 9 we have precisely similar results in the case of a series of glasses based on Kavalier's chemical glass, the silica being progressively replaced by boric oxide. The refractive-index curve also shows a maximum but the point of its occurrence is displaced compared with the curves of the other properties. In the

case of the chemical durability no advantage at any stage was found by substituting boric oxide for silica, the resistance to water and hydrochloric acid remaining constant for a certain concentration and thereafter rapidly breaking down. This reversal may possibly be due to the formation, in the early stages of the substitution of boric oxide for silica, of silicates in which part of the silica is replaced

FIG. 8.



by boric oxide. Further experimental work on this subject is in hand to endeavour to trace the cause satisfactorily.

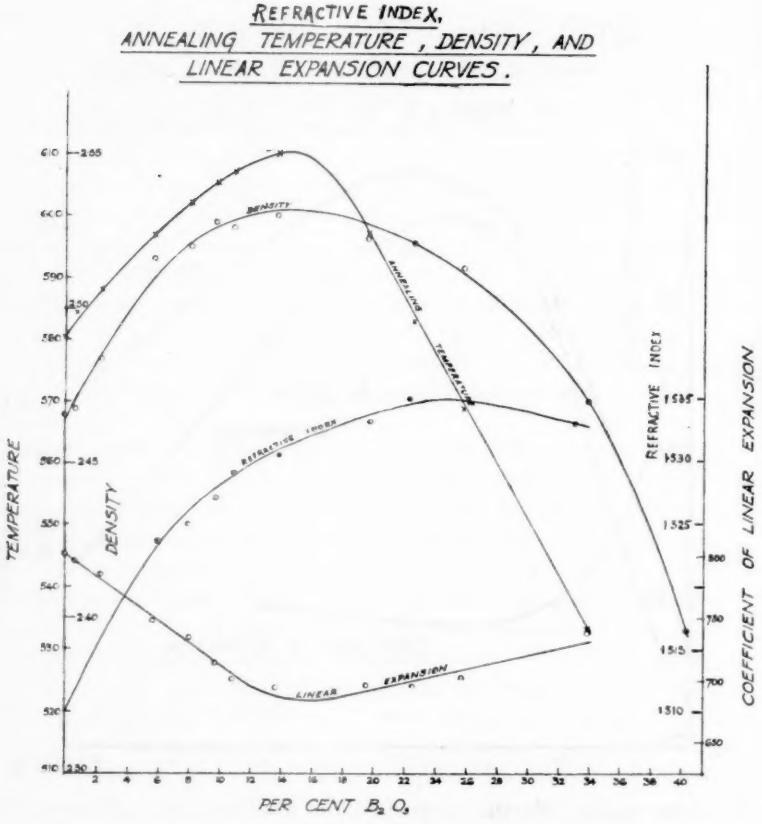
2. *The Influence of the Mode of Preparation of the Glass.*

The mode of preparation of the glass also has an influence on at least some of its physical properties. The prosecution of this problem by refined physical methods is only just beginning, but the facts now appear to admit of no doubt.

A particular glass may be produced by the melting of different

substances, many of which can be introduced in alternative forms. The alkaline elements may be introduced as carbonates or nitrates, for example. The alumina may be introduced as calcined alumina, hydrated alumina or through some mineral of known composition such as China clay, felspar, etc. One would expect the reactions on fusion to proceed to the same end. Chemical analysis, generally

FIG. 9.



speaking, shows that this is the case. We have found, however, that when glass is worked from the pot and drawn into tubing its working range (which depends on the rate of change of viscosity) is, in some cases, appreciably different according to the constituents from which the glass has been prepared. We have not yet detected such differences when simple salts serve as the basis for the glass mixture, except in so far as chlorides and sulphates almost invariably leave residues which influence the working properties. A distinct

difference is observed according as alumina is introduced in the simple form or as a mineral containing it. It is conceivable that when a mineral is employed a longer period is required to reach equilibrium, and this view is strengthened by the proof by Morey and Bowen [29] that orthoclase has an incongruent melting point and is slowly converted into leucite.

The presence of considerable amounts of water in the ingredients used in the glass-making mixture also has a definite effect on the working properties of the resulting glass. A soda–lime–silica or a potash–lead oxide–silica glass which has been melted from a wet batch mixture, that is, one containing 7, 8, 10 or more % of moisture, invariably sets more quickly than one produced from a dry batch mixture, although the composition of the resulting glass gives no clue to any difference of composition, and it has definitely been shown by us at Sheffield that in such cases the amount of water retained in the glass cannot exceed 0·05%. The influence of such factors was at first a matter of some surprise. Several investigations in which these influences were found to operate were reported to a Research Committee of the Glass Research Association and the results were regarded with some scepticism. I myself for a time was in doubt that the idiosyncrasies of the workman were not sufficient to account for this phenomenon. Becoming convinced, however, of the reality of these influences, I finally persuaded my colleagues on the Committee to accept them on the basis of further results obtained by putting the glass-worker through an examination in which pairs of glasses—in one or two cases the same, in other cases either of different composition or with one prepared from dry mixtures, the other from wet, and so on—were prepared, and the glass-maker only allowed to come into contact or have any knowledge whatever of the operation at the moment the glass was ready for manipulation. He was then asked to draw up a report on the working character of the glasses and to make suggestions as to the mixtures from which they had been made. His report, based entirely on the general manipulation of the glass, set out with astonishing accuracy the conditions under which the glasses had been prepared.

The remelting of glass is also accompanied by a shortening of its working range. At each melting it sets slightly more rapidly and becomes more brittle. There is no change in chemical composition to account for this quite marked change in viscosity or plasticity. In a series of glasses, made by us from mixtures of raw materials and previously melted glass, the working range of which was progressively shortened as the proportion of remelted glass in the mixture was increased, the extreme variation in the silica content was about

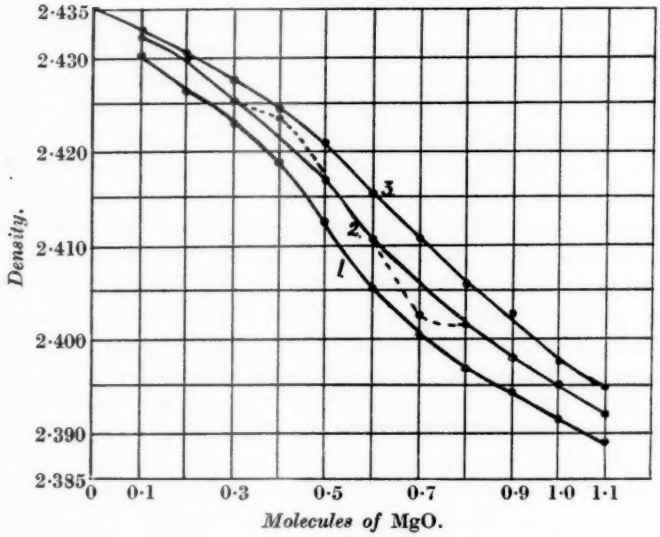
0·5 throughout the series, in the alumina 0·3, iron oxide 0·04, lime 0·3, and in the sodium oxide 0·36. Such variations make no difference which is observable when the glasses are melted from ordinary normally dry batch materials.

3. *The Influence of Heat Treatment.*

The subject of the heat treatment of glass has been one of the most interesting fields cultivated in the last few years. For example, we know that the state of annealing of glass influences the value of the

FIG. 10.

Effect of strain on density of glasses of general formula $6SiO_2(2-x)Na_2OxMgO$.



physical property. The density of strained glass is lower than that of annealed glass. Fig. 10 shows the results of experiments made by us [29a] on a series of soda–magnesia–silica glasses, the curve (3) representing the density when the glasses were annealed, and the lower curves being those determined from glass taken from slabs and rod in a strained condition.

The thermal expansion of glass may be from 3 to 6 or 7% higher if it is strained. The electrical properties are affected still more noticeably. Gray and Dobbie [3] found a potash–lead oxide–silica glass to be a much better insulator when annealed than when under strain and observed the following striking figures for the specific resistance :

Glass composition.			Temperature.	Specific resistance (ohms).
SiO_2.	PbO.	K_2O.		
48·2	40·8	10·6 (annealed)	140°	29,000
50·1	39·7	10·0 (unannealed)	142	1,329

Ferguson and Mulligan have found differences of as much as 100% in the specific electrical resistance of soda–lime–silica glass according as it was annealed or not. Berndt [29b] also found a difference in the compression strength according to the state of annealing as illustrated by the following data :

Glass : Borosilicate Crown.

Load.		Kg./cm.^{2} Mean.	Maximum.
Strain severe.	Continually increasing	15,000	18,400
	Increasing in steps	15,200	17,500
Well annealed.	Continually increasing	14,200	16,900
	Increasing in steps.....	12,500	15,100

A series of investigations carried out at the Bureau of Standards by Tool and collaborators [30] have shown that the density of glass can be made to vary according to the heat treatment it receives, the maximum variation so far obtained being between 1 and 2%. Simeon and Twyman [31] have shown that the refractive index can also be made to vary as much as 5 units in the third place of decimals by heat treatment, and the recovery of the original refractive index depends on both the temperature and the length of time at which the glass is reheated.

In Russia, Lebedev [31a] published in 1921 the results of investigations on several properties, including the refractive index, on very similar lines to those made by the workers at the Bureau of Standards, although entirely without knowledge of their work. Lebedev found a series of transition points in physical properties which occurred in the neighbourhood of 570°.

Although glass is regarded merely as a supercooled liquid, the physical changes in which are continuous, nevertheless Tool and Valasek [32] showed that a definite heat evolution or absorption occurs over a certain range when the glass is cooled or heated respectively. This is shown by the curve in Fig. 11 and it is similar in character to that of any transition from one solid phase to another. Over this same range, the coefficient of thermal expansion of glass undergoes a sudden increase, between 3 and 7 times that immediately preceding the change point, dependent on the composition of the glass. Fig. 12 shows this change in one of a series of soda–lime–silica glasses (74·52% SiO_2, 8·14 CaO, 16·86 Na_2O, 0·40 Al_2O_3) recently

Fig. 11.

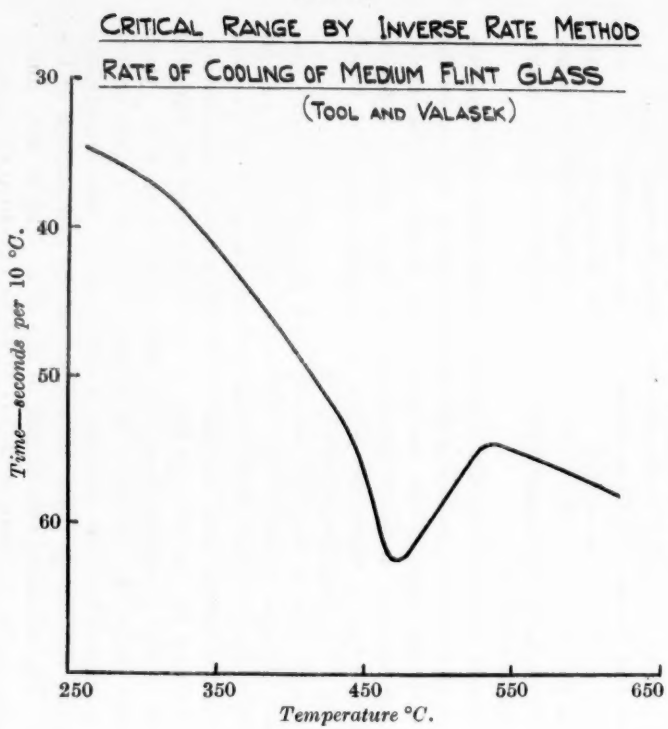
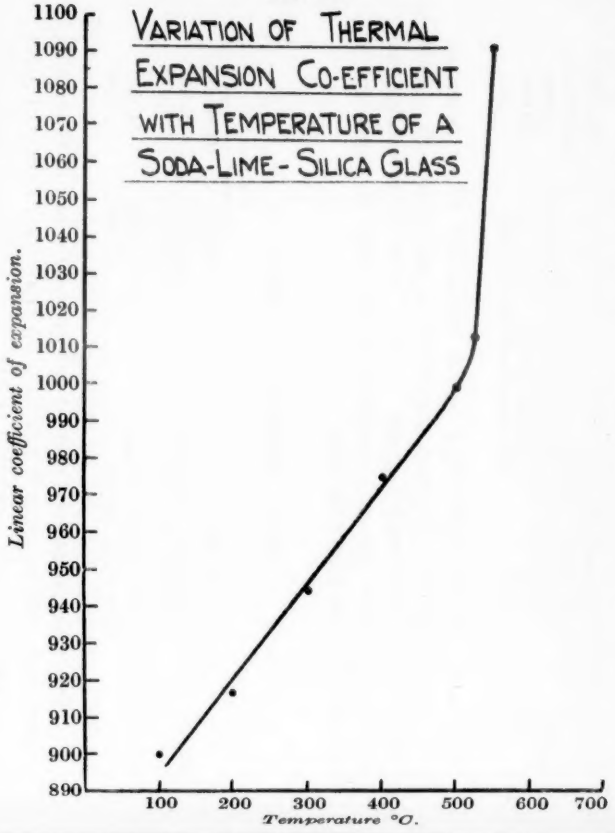

CRITICAL RANGE BY INVERSE RATE METHOD
RATE OF COOLING OF MEDIUM FLINT GLASS
(TOOL AND VALASEK)
Time—seconds per 10 °C.
30
40
50
60
250
350
450
550
650
Temperature °C.

Fig. 12.


VARIATION OF THERMAL EXPANSION CO-EFFICIENT WITH TEMPERATURE OF A SODA-LIME-SILICA GLASS
Linear coefficient of expansion.
1100
1090
1080
1070
1060
1050
1040
1030
1020
1010
1000
990
980
970
960
950
940
930
920
910
900
890
100
200
300
400
500
600
700
Temperature °C.

investigated by us. Samsoen [33] has found, in the case of boric oxide glass, a still bigger change, the mean linear coefficient up to 240° being less than 15×10^{-6}, whereas at 240—250° it exceeded 200×10^{-6}.

Lebedev put forward the theory that the heat effect was related to the inversion of the silica in the glass corresponding to the inversion temperature at 575° between α- and β-quartz. Tool and Valasek had found, however, that the borates and boric oxide showed a similar phenomenon, and recently Lebedev has withdrawn his hypothesis as obviously untenable. Tool was inclined to relate the magnitude of the heat effects to the tendency of the glasses to crystallisation. It seemed to me, however, that the phenomenon might be a general property of all amorphous forms of matter, and, to test this view, in 1923 some work was carried out by a student working under my direction to ascertain if common resin showed exothermic or endothermic effects. As a matter of fact no such effects were noted, and I understand that Dr. F. W. Preston, studying the properties of pitch over a wide range of temperature, also found no such thermal effects. Recently, however, Prof. le Chatelier has informed me, when contributing to the discussion of one of my papers, that he believes he has proved that these heat effects are actually associated with a definite change in all amorphous bodies. He states that changes similar to those which are observed in glasses at temperatures between 250° and 550° occur in other amorphous substances at a temperature which is dependent on the viscosity. The change point takes place between 0° and 100° for resins, pitch, and concentrated acrolein, and below 0° for viscous liquids, like glycerol, which have been solidified by cooling. Le Chatelier pictures the change as one dependent on the viscosity. As the temperature rises, he supposes, the molecules themselves swell but do not separate from one another. When once the internal friction has become sufficiently weak, the molecules begin to be spaced out and accordingly the coefficient of expansion greatly increases.

The study of glasses, therefore, promises to throw light on the nature and characteristics of the amorphous state. Instead of the old view of glasses and amorphous substances undergoing perfectly continuous changes in their properties from temperatures at which they are very fluid to those at which they are rigid, we have to recognise a discontinuity not essentially different from a change of state. It may be of some significance in this study that the biggest change recorded as occurring in the thermal expansion of a glass at the change point is that in boric oxide glass, a simple substance which has never yet been obtained in the crystalline form.

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CCLXXX.—*Optical Activity and the Polarity of Substituent Groups. Part IV.* sec.-β-*Octyl Esters of* o-, m-, *and* p-*Methoxy- and Nitro-benzoic Acids.*

By HAROLD GORDON RULE and ANNIE HUTTON NUMBERS.

IN previous communications it has been shown that the rotatory powers of derivatives of optically active alcohols reveal the existence of at least two distinct types of substituent effect. Among *l*-menthyl esters of mono-substituted acetic acids (Rule and Smith,

J., 1925, **127**, 2188) the influence of a number of simple substituents agrees closely with what has been termed the *general polar effect* of the groups, as observed in their influence on acidity, reaction velocity, and molecular inductive capacity (Rule and Paterson, *ibid.*, p. 2159).

Among the numerous menthyl esters of *o*-, *m*-, and *p*-substituted benzoic acids examined by Cohen, however, this relationship does not hold. In this case Cohen (J., 1914, **105**, 1895) observed that the facts could not be explained on the basis of Frankland's lever-arm theory, and drew the conclusion that the element or group lying nearest to the asymmetric atom produces the greatest effect, which according to the nature of the group may be an increase or decrease in rotation value, and that this value approaches the normal for the unsubstituted compound the further the substituent is removed from its proximity to the asymmetric group. It has recently been pointed out (Rule, J., 1924, **125**, 1122) that those *o*-substituents which raise the rotation of menthyl benzoate are *m*-directive in their effect on substitution in benzene, while those which depress the rotation are *o*-, *p*-directive, and that the relative effect of different substituents is in agreement with their relative polarity as deduced from the views of Sir J. J. Thomson and with their relative influence on benzene substitution as we pass from the strongly *m*-directive or positive nitro-group to the strongly *o*-, *p*-directive or negative fluoro-group (see also Rule and Smith, this vol., p. 553). A similar group effect appears to exist among certain simple aliphatic derivatives of active amyl alcohol.

Generally speaking, the esters of the cyclic alcohol, menthol, behave in a remarkably regular manner when examined from the point of view of optical activity. The majority of these compounds exhibit normal and apparently simple dispersion over the usual working range of wave-length, and their rotation undergoes little alteration with change of solvent and temperature. It was therefore considered of interest to investigate the influence of substituents on certain esters of *sec.*-β-octyl alcohol, since these compounds are known to be much more sensitive to alterations in molecular structure and external conditions (compare Pickard and Kenyon, J., 1914, **105**, 837; Hunter, J., 1924, **125**, 1389).

Esters of active octyl alcohol with *o*-, *m*-, and *p*-methoxybenzoic and nitrobenzoic acids have now been prepared, and their rotatory powers in the homogeneous state determined at temperatures between 20° and 95°. In the case of the methoxybenzoates, the values were measured for the D line and for the yellow, green, and violet mercury lines. Owing to the yellow colour of the nitro-derivatives, it was not found possible to obtain satisfactory readings

for these compounds with the violet line, but readings over the range λ_D to λ_{vi} were also taken using a 5% alcoholic solution. The values of $[M]_D$ and α_{vi}/α_D found for the esters at different temperatures are summarised in the following tables.* Figures referring to light of other wave-lengths and to other rotations in solution are given in the experimental portion of this paper.

I. *Molecular Rotations and Dispersion Ratios of the Homogeneous Esters.*

d-β-*Octyl Methoxybenzoates.*

	o-Compound.		*m*-Compound.		*p*-Compound.	
Temp.	$[M]_D$.	α_{vi}/α_D.	$[M]_D$.	α_{vi}/α_D.	$[M]_D$.	α_{vi}/α_D.
20°	+33·27°	1·513	+93·73°	2·084	+113·3°	2·147
40	37·31	1·663	92·77	2·086	112·2	2·149
60	40·82	1·770	91·61	2·090	111·0	2·150
80	44·00	1·852	90·42	2·096	110·0	2·149
90	45·38	1·895	89·82	2·097	109·4	2·151

$[M]_D$ for d-β-*Octyl Nitrobenzoates.*

	o-Compound.	*m*-Compound.	*p*-Compound.
Temp.	$[M]_D$.	$[M]_D$.	$[M]_D$.
20°	+121·6°	+107·8°	(30°) 117·8°
40	119·6	104·2	115·9
60	117·6	101·0	112·3
80	116·1	98·2	109·6
90	115·4	97·0	108·8

For *d*-β-octyl benzoate Pickard and Kenyon (J., 1915, **107**, 122) find $[M]_D^{20°} = +77·84°$.

Rotations of Nitrobenzoic Esters in 5% *Alcoholic Solution (at about* 20°).

o-Compound.		*m*-Compound.		*p*-Compound.	
$[M]_D$.	α_{vi}/α_D.	$[M]_D$.	α_{vi}/α_D.	$[M]_D$.	α_{vi}/α_D.
155·8°	2·698	103·1°	2·047	120·2°	2·123

Dispersion.

When the reciprocal of the rotation is plotted against the square of the wave-length, a straight line is obtained for the homogeneous *m*-methoxy-compound at all temperatures and for the *p*-methoxy-compound at the two lower temperatures of experiment. It may therefore be concluded that the dispersion of these esters under the conditions stated is normal and apparently simple. The *o*-methoxy-ester exhibits complex dispersion, which is especially

* These values are read off from the smooth curves drawn from the experimental figures. In every instance the sign of the rotation is the same as that of the active alcohol from which the ester is derived, and to avoid confusion certain values determined for *l*-esters are here tabulated—with change of sign—under the corresponding *d*-compounds.

marked at the lower temperatures employed, and the dispersions of the *o*-nitro-compound also are complex, although the graphs of $1/\alpha$ against λ^2 for the *m*- and *p*-isomerides in alcoholic solution approximate very closely to straight lines.

Both *o*-derivatives have abnormal dispersion ratios, the value of α_{vi}/α_D for the *o*-methoxy-ester being below and that for the *o*-nitro-ester above the value for the respective *m*- and *p*-compounds.

Influence of Substituents.

As may be seen from the above figures, the introduction of a methoxy-group into the *o*-position in the benzene nucleus leads to a marked depression in the rotatory power of octyl benzoate, whereas a nitro-group in the same position results in a considerable increase. As in the case of menthyl benzoate,* therefore, the *o*-, *p*-directive group produces a depression and the *m*-directive group an exaltation of rotatory power.

In the *m*- and *p*-positions both substituents bring about a rise in the rotatory power of the octyl ester, thus contrasting strongly with their behaviour in the menthyl compound, in which the effect of *m*- and *p*-substituents is in most cases negligible.

The values for the *o*-, *m*-, and *p*-derivatives are neither in agreement with Frankland's lever-arm hypothesis nor with the electrostatic modification of the latter suggested by one of us; nor do they lend support to the conclusion arrived at by Cohen (*loc. cit.*) from a study of the menthyl benzoates. It might be expected that the close relationship existing in certain cases between the influence of substituents on optical activity and acidity (Betti, *Gazzetta*, **1923**, **53**, 417; Rule and Smith, *loc. cit.*) would also be evident in the octyl benzoates, particularly among the *m*- and *p*-derivatives, in which the strong specific effect of the *o*-group is absent. A comparison of the rotatory powers of the esters with the dissociation constants of the corresponding nitro- and methoxy-benzoic acids (quoted below) shows that the powerfully acidic nitro-group affects

	o.	*m*.	*p*.
NO_2	0·62	0·035	0·040 (benzoic acid, $k = 0·0068$).
OMe	0·0082	—	0·0033

rotation and acidic strength qualitatively in the same manner, *viz.*, $o\text{-}NO_2 > p\text{-}NO_2 > m\text{-}NO_2 > H$, although for the resemblance to be complete the rotation of the *o*-nitro-ester should be much higher

* The rotations of the menthyl esters of α- and β-naphthoic acids are depressed in a similar manner by the introduction of a methoxy-group in the *o*-position to the carboxylic complex (compare Cohen and Dudley, J., 1910, **97**, 1750).

than that found.* This agreement does not extend to the very weakly acidic methoxy-group, which gives for rotatory powers the sequence *p*-OMe>*m*-OMe>H>*o*-OMe and for acidic strength *o*-OMe>H>*p*-OMe. It is remarkable that in the *p*-position the otherwise dissimilar nitro- and methoxy-groups produce the same pronounced increase in rotation.

An example of a different type which exhibits some points in common with the above is that of the substituted benzoylcarvoximes (Goldschmidt and Freund, *Z. physikal. Chem.*, 1894, **14**, 398).

Molecular Rotations of Substituted Benzoylcarvoximes (*in chloroform solution*).

Substit.	*o*-.	*m*-.	*p*-.	Substit.	*o*-.	*m*-.	*p*-.
Br	90·3	63·5	51·8	H	—	71·7	—
Me	76·6	76·0	66·3	NO_2	0	64·9	54·4

Here the *m*-directive nitro-group lowers the rotation when introduced into the *o*-position, and the *o*-, *p*-directive bromo- and methyl groups raise the value. The methyl group also increases the rotation in the *m*-position, but otherwise all *m*- and *p*-substituents depress the rotatory power. The case is thus closely analogous to that of the octyl benzoates, except that the changes are in the reverse direction. In passing, it may be noted that the relative influence of the different *o*-substituents, Br>Me>H>NO_2, is in agreement with their relative polarity and their relative influence on the substitution of benzene.

In general, the molecular rotations of the octyl esters fall with rise of temperature, as may be seen from the figures given in Table I. An exception is found in the *o*-methoxy-ester, the rotation of which increases with rise of temperature.

Experimental.

The active *sec.*-β-octyl alcohol required for this investigation was prepared from the racemic alcohol by the method of Pickard and Kenyon (J., 1907, **91**, 2058) as modified later by Kenyon (J., 1922, **121**, 2540). It had $[\alpha]_D^{16} = \pm 8{\cdot}14°$.

The esters were obtained from the corresponding acids by way of the acid chlorides, the combination of the latter with active alcohol being carried out in the presence of pyridine as a condensing agent. Purification was effected by fractionating the crude esters until of constant rotatory power. In general it was found that no further change in rotation occurred after the first fractionation.

* The relatively high rotation of the *o*-isomeride is much more evident in alcoholic solution, especially when values for λ_{vi} are compared.

l-β-*Octyl* o-*methoxybenzoate* was prepared from *o*-methoxybenzoic acid obtained by the oxidation of pure *o*-tolyl methyl ether. It is a colourless, odourless liquid, b. p. 187·5°/13 mm. (Found : C, 72·6; H, 9·2. $C_{16}H_{24}O_3$ requires C, 72·7; H, 9·2%).

l-β-*Octyl* m-*methoxybenzoate* was obtained in a similar manner to the *o*-compound from *m*-tolyl methyl ether, which was oxidised to *m*-methoxybenzoic acid at the ordinary temperature by a 2½% solution of potassium permanganate (compare Oppenheim and Pfaff, *Ber.*, 1875, **8**, 887). The acid was purified by repeated crystallisation from ligroin till it melted sharply at 106°. The ester is a colourless, odourless liquid, b. p. 187·5°/12 mm. (Found : C, 72·6; H, 9·3. $C_{16}H_{24}O_3$ requires C, 72·7; H, 9·2%).

l-β-*Octyl anisate* (from anisic acid) is a colourless, odourless liquid, b. p. 189°/13 mm. (Found : C, 72·5; H, 9·2. $C_{16}H_{24}O_3$ requires C, 72·7; H, 9·2%).

l-β-*Octyl* o-*nitrobenzoate* was prepared from *o*-nitrobenzoyl chloride (Kahlbaum). The pale yellow ester is odourless, and boils at 204°/15 mm. (Found : C, 64·5; H, 7·8; N, 5·2. $C_{15}H_{21}O_4N$ requires C, 64·5; H, 7·6; N, 5·0%).

l-β-*Octyl* m-*Nitrobenzoate*.—The starting point in the preparation of this ester was *m*-nitrobenzaldehyde, which was purified by recrystallisation from ligroin. The *m*-nitro-ester was obtained as a pale yellow, odourless liquid, b. p. 212°/18 mm. (Found : C, 64·6; H, 7·6; N, 5·3. $C_{15}H_{21}O_4N$ requires C, 64·5; H, 7·6; N, 5·0%).

l-β-*Octyl* p-*nitrobenzoate* (from Kahlbaum's *p*-nitrobenzoyl chloride) is a pale yellow solid at the ordinary temperature. It was recrystallised from alcohol till of constant rotation. M. p. 29·5—30° (Found : C, 64·5; H, 7·7; N, 5·3%).

Densities and Rotatory Powers of the Esters in the Homogeneous State.

All rotations were measured in a 50 mm. tube. Densities were determined with the aid of a pyknometer holding between 3 and 4 c.c.

Observed Densities and Rotations.

l-β-Octyl *o*-methoxybenzoate.

$D_4^{t°}$	1·0004 at 20·3°	0·9824 at 42·4°	0·9699 at 57·9°	0·9513 at 81·35°.
α_D	6·48° at 24·4°	6·94° at 39·6°	7·38° at 55°	8·14° at 92·1°.
α_{Ye}	6·60° at 24·4°	7·14° at 39·6°	7·67° at 55°	8·49° at 92·1°.
α_{Gr}	7·32° at 24·4°	7·95° at 39·6°	8·58° at 55°	9·51° at 92·1°.
α_{Vl}	10·01° at 24·4°	11·45° at 39·6°	12·95° at 55°	15·48° at 92·1°.

l-β-Octyl *m*-methoxybenzoate.

$D_4^{t°}$	0·9939 at 20·42°	0·9771 at 41·6°	0·9641 at 58·2°	0·9464 at 80·45°.
α_D	17·63° at 20·4°	17·24° at 37·1°	16·44° at 68·5°	15·90° at 92·9°.
α_{Ye}	18·43° at 20·4°	18·03° at 37·1°	17·17° at 68·5°	16·59° at 92·9°.
α_{Gr}	21·04° at 20·4°	20·62° at 37·1°	19·64° at 68·5°	19·02° at 92·9°.
α_{Vl}	36·76° at 20·4°	36·05° at 37·1°	34·52° at 68·5°	33·33° at 92·9°.

l-β-Octyl *p*-methoxybenzoate.

$D_4^{t°}$	0·9940 at 23·9°	0·9807 at 41°	0·9677 at 57·9°	0·9488 at 81·8°.
α_D	21·33° at 21·5°	20·87° at 39°	20·22° at 65·4°	19·42° at 93·7°.
α_{ye}	22·33° at 21·5°	21·88° at 39°	21·08° at 65·4°	20·23° at 93·7°.
α_{gr}	25·56° at 21·5°	25·05° at 39°	24·16° at 65·4°	23·21° at 93·7°.
α_{vl}	45·81° at 21·5 ;	44·80° at 39°	43·26° at 65·5°	41·75° at 93·7°.

l-β-Octyl *o*-nitrobenzoate.

$D_4^{t°}$	1·0701 at 24·2°	1·0560 at 41·8°	1·0407 at 61·1°	1·0234 at 82·5°.
α_D	23·26° at 23·5°	22·70° at 38·3°	21·77° at 65°	20·98° at 92·2°.
α_{ye}	24·54° at 23·5°	23·90° at 38·3°	22·96° at 65°	21·97° at 92·2°.
α_{gr}	28·88° at 23·5°	28·07° at 38·3°	26·92° at 65°	25·90° at 92·2°.

d-β-Octyl *m*-nitrobenzoate.

$D_4^{t°}$	1·0725 at 24·1°	1·0587 at 41°	1·0453 at 57·4°	1·0238 at 83·8°.
α_D	20·77° at 20·0°	19·81° at 39°	19·07° at 55·7°	17·53° at 94°.
α_{ye}	21·68° at 20·0°	20·76° at 39°	20·00° at 55·7°	18·40° at 94°.
α_{gr}	24·88° at 20·0°	23·63° at 39°	22·79° at 55·7°	21·01° at 94°.

d-β-Octyl *p*-nitrobenzoate.

$D_4^{t°}$	1·0631 at 32·9°	1·0471 at 52·75°	1·0384 at 63·25°	1·0248 at 80·1°.
α_D	22·00° at 39·1°	21·05° at 58·4°	20·22° at 76·5°	19·75° at 91·9°.
α_{ye}	22·99° at 39·1°	22·02° at 58·4°	21·21° at 76·5°	20·64° at 91·9°.
α_{gr}	26·44° at 39·1°	25·27° at 58·4°	24·22° at 76·5°	23·65° at 91·9°.

II. *Specific Rotations of the Esters in the Homogeneous State.*

(For values of $[M]_D$ and α_{vl}/α_D see Table I.)

l-β-Octyl *o*-methoxybenzoate.

t.	$D_4^{t°}$.	$[\alpha]_D$.	$[\alpha]_{ye}$.	$[\alpha]_{gr}$.	$[\alpha]_{vl}$.
20°	1·0006	−12·59°	−12·93°	−14·23°	−19·05°
40	0·9844	14·12	14·59	16·25	23·47
60	0·9683	15·45	16·07	17·97	27·35
80	0·9523	16·66	17·37	19·45	30·85
90	0·9443	17·18	17·94	20·08	32·55

l-β-Octyl *m*-methoxybenzoate.

20	0·9945	−35·48	−37·08	−42·33	−73·97
40	0·9785	35·11	36·65	41·90	73·27
60	0·9627	34·67	36·19	41·40	72·50
80	0·9467	34·23	35·70	40·94	71·77
90	0·9389	34·00	35·47	40·67	71·32

l-β-Octyl *p*-methoxybenzoate.

20	0·9968	−42·88	−44·90	−51·38	−92·07
40	0·9814	42·47	44·43	50·89	91·26
60	0·9661	42·03	43·93	50·31	90·36
80	0·9503	41·63	43·44	49·84	89·49
90	0·9427	41·39	43·20	49·52	89·02

l-β-Octyl *o*-nitrobenzoate.

t.	$D_4^{t°}$.	$[\alpha]_D$.	$[\alpha]_{ye}$.	$[\alpha]_{gr}$.
20°	1·0735	−43·56°	−46·00°	−54·18°
40	1·0571	42·82	45·15	52·97
60	1·0410	42·15	44·38	52·03
80	1·0251	41·60	43·68	51·33
90	1·0172	41·35	43·33	51·08

d-β-Octyl *m*-nitrobenzoate.

20	1·0758	+38·61°	+40·31°	+46·25°
40	1·0594	37·32	39·12	44·59
60	1·0430	36·18	37·97	43·17
80	1·0266	35·18	36·92	42·02
90	1·0185	34·74	36·45	41·53

d-β-Octyl *p*-nitrobenzoate.

30	1·0655	+42·20°	+44·04°	+50·94°
40	1·0573	41·52	43·43	49·88
60	1·0410	40·21	42·15	48·24
80	1·0249	39·24	41·12	47·05
90	1·0168	38·97	40·75	46·68

III. *Rotations of Octyl Nitrobenzoates in Alcoholic Solution (approx. 5%).*

	o-Ester (5·0900 g. in 100 c.c.). *l* 50 mm.		*m*-Ester (5·1436 g. in 100 c.c.). *l* 200 mm.		*p*-Ester (5·0652 g. in 100 c.c.). *l* 200 mm.	
	$\alpha^{20·8°}$.	[α].	$\alpha^{20·2°}$.	[α].	$\alpha^{22·3°}$.	[α].
α_D	1·42°	55·80°	3·80°	36·94°	4·36°	43·04°
α_{Ye}	1·69	66·40	3·99	38·79	4·60	45·41
α_{gr}	1·90	74·65	4·51	43·84	5·19	51·23
α_{vl}	3·83	150·5	7·78	75·63	9·38	92·59

The authors gratefully acknowledge their indebtedness to the Earl of Moray Research Fund for a grant which has covered most of the expense incurred in this investigation.

UNIVERSITY OF EDINBURGH. [*Received, April 16th*, 1926.]

CCLXXXI.—*Conessine.*

By DARAB DINSHA KANGA, PANCHANDANA RAMASWAMI AYYAR, and JOHN LIONEL SIMONSEN.

THE alkaloid conessine has been obtained from the bark and seeds of *Holarrhena antidysenterica* and from the bark of *H. africana* and *H. congolensis*. It has formed the subject of a considerable number of communications,* but little is known regarding its chemistry beyond the fact that it has the empirical formula $C_{24}H_{40}N_2$ and contains two tertiary –NMe groups.

We had planned an extended investigation on this alkaloid, since, in addition to the intrinsic value attaching to the determination of

* The following would appear to be a complete list of the references to conessine in the literature: Haines (*Trans. Med. Soc. Bombay*, 1858, **4**, 28, as nereine); Stenhouse (*Pharm. J.*, 1864, **5**, 493); Haines (*ibid.*, 1865, **6**, 432); Wulfsberg (*Gött. Nachr.*, 1878, No. 3); Keidel, *Dissert.*, Göttingen, 1878 ("Physiologische Wirkung des Conessine"); Dutt (Calcutta Chemical Examiner's Report, 1880); Warnecke (*Ber.*, 1886, **19**, 60); Polstorff and Schirmer (*ibid.*, p. 78); Polstorff (*ibid.*, p. 1682); Blondel (*J. Pharm. Chem.*, 1887, **16**, 391); Warnecke (*Arch. Pharm.*, 1888, **226**, 248, 281); Ulrici (*ibid.*, 1918, **256**, 57); Giemsa and Halberkann (*ibid.*, p. 201); Pyman (J., 1919, **115**, 163).

its constitution, there was the added interest that there is a considerable body of clinical evidence indicating that the bark of *H. antidysenterica* is of value in the treatment of diseases of the dysenteric type (compare Henry and Brown, *Trans. Roy. Soc. Trop. Med. Hyg.*, 1923–4, **17**, 61, 381). Unfortunately our experiments had to be terminated at an early stage, as certain derivatives of conessine had an extremely toxic effect on one of us (J. L. S.), giving rise to a severe attack of Giant Urticaria. We prepared a few new derivatives of conessine, and record the results of our work in the hope that they may be of assistance to other investigators.

Giemsa and Halberkann observed (*loc. cit.*, p. 212) that when the ammonium base formed by treating an aqueous solution of conessine dimethiodide with silver oxide was heated at 200° under diminished pressure, trimethylamine was evolved, leaving a crystalline base. We have examined this reaction in some detail and have found the residue to consist of a mixture of at least two bases. One of these, for which the name apo*conessine* is proposed, has the formula $C_{22}H_{33}N$, having been formed by the elimination of trimethylamine, water and methyl alcohol from conessinedimethylammonium hydroxide. It was characterised by the preparation of the crystalline *hydrogen sulphate* and *picrate*. The crystalline *methiodide* was reconverted into the original base on treatment with silver oxide.

We have also made some preliminary experiments on the action of alkali on conessine dimethosulphate and obtained a very hygroscopic, crystalline base, $C_{26}H_{44}N_2$; this is apparently a dimethyl derivative of conessine formed by the loss of 2 mols. of water from the ammonium base which is evidently the first product of the reaction.

In the preparation of conessine dimethosulphate (compare Giemsa and Halberkann, *loc. cit.*), in addition to the crystalline dimethosulphate, a thick, extremely hygroscopic oil was obtained which, on treatment with alkali, gave a *base* for which a simple formula could not be found; possibly this was due to the presence of some impurity, but we could not repeat the preparation.

Experimental.

The finely-crushed seeds of *H. antidysenterica* (500 g.) were extracted in a copper Soxhlet apparatus with light petroleum (b. p. 40—60°) to remove the fixed oil (19%), and having been freed from solvent by a current of air, were mixed with milk of lime (CaO, 100 g.). The whole was exposed to the air over-night and then extracted with 88% alcohol for about 18 hours. The deep brown extract was freed from alcohol by distillation, finally under

diminished pressure, and the residue shaken with dilute hydrochloric acid. Ether removed non-basic impurities from the filtered acid solution, from which ammonia then precipitated the crude alkaloid. This was extracted with ether, and from the dried extract the alkaloid was obtained as a viscid, brown oil which partly crystallised on keeping (yield 1%). The oil, dissolved in the minimum quantity of alcohol, was warmed with a concentrated alcoholic solution of sufficient oxalic acid for the formation of the hydrogen oxalate. The salt crystallised in colourless prisms on cooling and was recrystallised from alcohol.* The recovered base melted at 120—121°, and at 125° after crystallisation from acetone (Found: C, 80·6; H, 11·4. Calc.: C, 80·0; H, 11·3%).

Conessine was not attacked when boiled in sulphuric acid solution for some time with manganese dioxide. It was, however, slowly converted by an acetic acid solution of mercuric acetate into a base which crystallised from dilute alcohol in fine needles. This reaction would appear to be worthy of further investigation.

apo*Conessine*.—A solution of conessine dimethiodide (35 g.) in water (400 c.c.) was shaken with an excess of freshly-precipitated silver oxide, the silver iodide and the excess of the oxide were removed, and the colourless filtrate was evaporated on the water-bath. The concentrated, faintly yellow solution was heated under diminished pressure, finally at 200°, vigorous frothing taking place. The deep brown, viscid oil thus obtained was dissolved in chloroform, filtered from a little carbonaceous matter, and the solvent removed. The residual oil on trituration with a little alcohol rapidly crystallised, and on recrystallisation from absolute alcohol apo*conessine* was obtained in needles several centimetres in length; m. p. 68·5° (Found: C, 84·9; H, 10·6; N, 5·0. $C_{22}H_{33}N$ requires C, 84·9; H, 10·6; N, 4·5%). This base is insoluble in water, very sparingly soluble in cold alcohol, and more readily soluble in hot. It is readily soluble in benzene, chloroform, or ethyl acetate, and somewhat readily soluble in light petroleum. Its port-wine coloured solution in concentrated sulphuric acid becomes colourless on the addition of water. It dissolves in nitric acid with a deep red colour, which rapidly changes to yellow.

The *hydrochloride* and *hydrobromide* were sparingly soluble, amorphous solids; the *hydrogen sulphate*, which was readily soluble in hot water, much more sparingly soluble in cold, crystallised in glistening leaflets, m. p. 107—108°. The salt crystallised apparently

* Since crystallisation of the base from acetone is always accompanied by considerable loss of material, when working with large quantities it is more convenient to recrystallise the hydrogen oxalate; the base is then readily obtained pure enough for experimental purposes and does not require to be recrystallised.

with $7\frac{1}{2}$ mols. of water of crystallisation (Found: H_2O, 11·0. $C_{22}H_{33}N,H_2SO_4,7\frac{1}{2}H_2O$ requires $3\frac{1}{2}H_2O$, 11·6%), $3\frac{1}{2}$ of which were lost on drying in a vacuum (Found: S, 6·4. $C_{22}H_{33}N,H_2SO_4,4H_2O$ requires S, 6·6%). After drying, the salt began to soften at 138°, gradually darkened and decomposed, but was not completely liquid at 280°.

The *picrate* crystallised from alcohol in fine, yellow needles, m. p. 110—111° (Found: C, 62·0; H, 7·0. $C_{28}H_{36}O_7N_4$ requires C, 62·2; H, 6·7%). The *methiodide* was prepared by heating a mixture of the base (1 g.), methyl alcohol (5 c.c.), and methyl iodide (1 g.) in a sealed tube at 100° for 3 hours. It separated on cooling, and more was obtained on evaporation of the mother-liquor. It crystallised from ethyl acetate–methyl alcohol in prismatic needles; these sintered at 245° to a viscid resin which became clear at 283—285° (Found: I, 28·1. $C_{23}H_{36}NI$ requires I, 28·0%). When the methiodide was treated with silver oxide in aqueous solution, *apo*conessine was re-formed.

The alcoholic filtrate from which *apo*conessine had been separated (see p. 2125) yielded, on removal of the solvent, a viscid, uncrystallisable oil. This was dissolved in an excess of dilute hydrochloric acid (1 : 2), the small quantity of *apo*conessine hydrochloride that separated was filtered off, and the base recovered from the filtrate. It had b. p. 253—255°/11 mm. and was a faintly yellow oil which slowly crystallised at 0° in fine needles. It was readily soluble in all the ordinary solvents and its aqueous solution showed very strong fluorescence. The salts with organic and inorganic acids were readily soluble in water. The picrate was obtained crystalline from ethereal solution, but it was not possible to investigate this method of purification.

Conessine Dimethosulphate.—The base (5 g.) and methyl sulphate (5·6 g.) reacted so vigorously in methyl alcohol (5 c.c.) that the mixture boiled. After about 5 minutes the dimethosulphate began to crystallise in well-formed prisms and after 1 hour acetone (5 c.c.) was added and the crystalline solid collected (yield 6·3 g.); more was obtained (2·6 g.) on evaporating the mother-liquor in a vacuum. The filtrate, after complete removal of the solvent, yielded a viscid, semi-crystalline oil which was extremely hygroscopic and resisted all attempts at purification. The dimethosulphate, after repeated crystallisation from methyl alcohol–acetone, was obtained in glistening prisms which softened at 225° and melted at 240—242° with slight darkening but no decomposition. The prisms effloresced when dried over sulphuric acid (Found: S, 10·6. Calc.: S, 10·5%).

Action of Potassium Hydroxide on Conessine Dimethosulphate.—The dimethosulphate (6·3 g.) and potassium hydroxide (2·5 g.)

in aqueous solution were heated on the water-bath, a slow stream of air being passed over the solution and through an absorption apparatus containing dilute hydrochloric acid. The hydrochloric acid solution, on subsequent evaporation, yielded no residue, and apparently no volatile base was formed. After 3 hours the pale brown alkaline solution was concentrated on the water-bath; a small amount of a brown oil then separated which was removed in chloroform. (The extract on evaporation yielded 0·5 g. of a brown resin which was not examined.) The aqueous solution, now colourless, was saturated with carbon dioxide and evaporated first on the water-bath and finally to dryness in a vacuum desiccator over sulphuric acid. The crystalline residue was ground with methyl alcohol, the solution filtered from inorganic matter, and the solvent removed, the treatment being repeated until the crystalline residue was completely soluble in cold methyl alcohol.

The *base* remaining after the removal of the alcohol crystallised in needles, but was extremely hygroscopic. It was insoluble in benzene, very sparingly soluble in acetone, readily in methyl alcohol or water. It gave a *dipicrate* which separated from dilute acetone in fine, yellow needles, m. p. 258—259° (slight decomp.) (Found : C, 54·2, 54·2; H, 5·9, 6·1; N, 13·8. $C_{38}H_{50}O_{14}N_8$ requires C, 54·1; H, 5·9; N, 13·3%). The *dimethiodide* crystallised from hot water in glistening concentric groups of needles when the solution was rapidly cooled, but on slow cooling or evaporation well-formed prisms were deposited. The dimethiodide did not melt at 290°.

The hygroscopic oil obtained during several preparations of the dimethosulphate (see p. 2126) was treated with potassium hydroxide in the way described above. The viscid, brown oil that separated from the concentrated aqueous solution was taken up with chloroform. On removal of the solvent a crystalline solid remained which, after repeated crystallisation from acetone–benzene, was obtained in colourless, silky needles; these rapidly became brown on exposure to the air. As only a small quantity of material was available, it is possible that the substance was not obtained quite free from the large amount of resinous impurity which accompanied it. It melted at 253—254° after sintering at 251°, was readily soluble in water, and its aqueous solution showed a marked fluorescence (Found : C, 63·9, 63·7; H, 8·7, 8·8; N, 9·7%). The *picrate* crystallised from alcohol in small, yellow plates, decomp. about 256°, but it was not prepared in sufficient quantity for analysis.

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[*Received, May 3rd,* 1926.]

CCLXXXII.—*The Chemistry of the Three-carbon System. Part VI. Some Systems containing the Benzoyl Group.*

By MAURICE DUNCAN FARROW and GEORGE ARMAND ROBERT KON.

FROM the analogy existing between compounds containing the keto-enol and the three-carbon system (J., 1923, **123**, 1361) it is possible to predict a similarity in the behaviour of the compounds under the influence of factors affecting the mobility or point of equilibrium of such systems. For example, the introduction of a benzoyl group in the place of acetyl in various diacylmethanes produces a greater tendency to enolisation and enhances the acidity of the compound (K. H. Meyer, *Ber.*, 1912, **45**, 2843; Dieckmann, *Ber.*, 1922, **55**, 2470); the phenylated compounds also show a greater tendency to crystallise and therefore are more readily separated into the pure keto and enol forms by freezing, etc. The introduction of benzoyl as an activating group in compounds which owe their mobility to the three-carbon system should give rise to a series of ketones possessing considerable mobility, since this property is clearly connected with the acidity or "enolising efficiency" of the activating group (compare Meyer, *loc. cit.*). The enhanced tendency to enolisation should be detectable in the more ready formation of alkyl derivatives, particularly in view of the results already obtained (Kon, this vol., p. 1792). Moreover, it was hoped that the new ketones would prove useful in the separation of the two constituents of an equilibrium mixture of the nature of *cyclo*hexenylacetone; pending further work on this problem, it is proposed to describe the general properties of ketones of the new series.

The compounds prepared include α-Δ^1-*cyclo*hexenylacetophenone (I), α-Δ^1-*cyclo*pentenylacetophenone (II), and the corresponding ketones of the *gem*-diethyl series (III and IV).

(I.) $CH_2<\begin{matrix}CH_2\cdot CH_2\\ CH_2-CH\end{matrix}>C\cdot CH_2\cdot COPh$ $\quad$ $\begin{matrix}CH_2\cdot CH_2\\ CH_2-CH\end{matrix}>C\cdot CH_2\cdot COPh$ (II.)

(III.) $\begin{matrix}Et\\ Et\end{matrix}>C{:}CH\cdot COPh$ $\quad$ $\begin{matrix}Et\\ CHMe\end{matrix}>C\cdot CH_2\cdot COPh$ (IV.)

Except for a few minor differences attributable to the effect of the phenyl group, the properties of these compounds closely resemble those of the corresponding methyl ketones, in accordance with theoretical considerations; the compounds (III) and (IV) exhibit what was described as retarded mobility (Kon and Linstead, J., 1925, **127**, 815).

The effect of the phenyl group is apparent in the optical properties

of the ketones, which all show exaltation of the molecular refraction; this must be due to the fact that the double bond of the keto-group is conjugated with those of the phenyl group. A similar if less pronounced exaltation is observed in acetophenone, from which these compounds may be considered to be derived. The unsatisfactory agreement of the observed and calculated figures for the refraction does not affect the value of the optical method, because comparisons can be made between the optical properties of a series of closely related compounds which agree amongst themselves, thus eliminating the theoretical figures altogether. As regards the tendency to enolisation, there is evidence to show that here again the phenyl group exercises an influence, for the yield of α-ethyl derivatives from the ketones (I) and (II) is much higher than in the case of *cyclo*hexenylacetone. In view of the high enolising efficiency of the group —COPh, it might have been expected that the ketones (I) and (II) could be methylated in the presence of methyl alcohol (compare Kon, *loc. cit.*), but this was not the case.

As already stated, these differences are of a minor character; the most striking characteristics of this series of compounds are due to the three-carbon system which they contain and in this respect they differ but little from the corresponding methyl ketones.

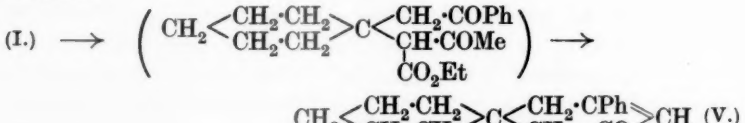
The reactions of the compound (I) make it clear that, although it has only been obtained in one form, to which the βγ-structure has been assigned, it functions as an equilibrium mixture of the αβ- and the βγ-phases:

$$CH_2<\begin{matrix}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{matrix}>C{:}CH\cdot COPh \rightleftharpoons CH_2<\begin{matrix}CH_2\cdot CH_2\\CH_2-CH\end{matrix}>C\cdot CH_2\cdot COPh$$

αβ. βγ.

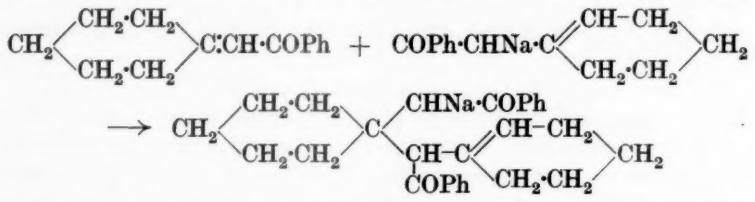
The compound (I) was readily prepared by the direct condensation of *cyclo*hexanone with acetophenone; it could also be obtained by the action of magnesium phenyl bromide or, better, its double compound with zinc chloride (Blaise, *Bull. Soc. chim.*, 1911, **9**, 9) on either Δ^1-*cyclo*hexenylacetyl chloride or *cyclo*hexylideneacetyl chloride. In spite of careful manipulation, no difference could be detected between the products of these two reactions; and it has been previously shown that the two solid acids (m. p. 38° and 92°, respectively) can be regenerated from these acid chlorides. The same semicarbazone, m. p. 120—121°, was obtained in good yield from the ketone derived from each of these sources; exhaustive fractional crystallisation of the semicarbazone failed to reveal the existence of a second modification such as was isolated from *cyclo*hexenyl- and from *cyclo*pentenyl-acetone. Oxidation with ozone led to an acidic oil having the properties of an aldehyde and giving

a quantitative yield of benzoic acid on hydrolysis; unfortunately no other definite fission-products could be isolated. No *cyclo*hexanone, which would result from the oxidation of the αβ-phase of the compound, could be detected. The ketone did not react smoothly with ethyl sodiomalonate, whilst the reaction with ethyl sodiocyanoacetate was followed by fission, acetophenone being one of the products isolated; the existence of the αβ-phase of the ketone was, however, definitely proved by the reaction with ethyl sodioacetoacetate, a compound (V) analogous to *iso*phorone being obtained :

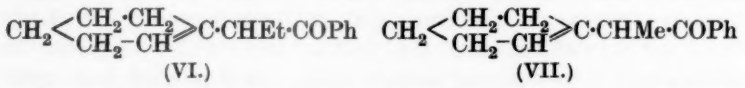


The reaction takes a long time to complete and the yield never exceeds 50%, but the ketone recovered from the operation can be condensed again with the same result.

Another interesting reaction is brought about by the agency of cold sodium ethoxide; only a tenth of the ketone remains unchanged after 24 hours, the remainder being changed to a solid, $C_{28}H_{32}O_2$, m. p. 201°, which readily loses a molecule of water, giving another solid, m. p. 106°. It would appear that the first substance was formed by the condensation of the αβ-phase of the ketone (I) with the sodio-derivative of the βγ-phase, the reaction being



analogous to that observed with ethyl α-cyanodimethylacrylate (Birch and Kon, J., 1923, **123**, 2440); the compound can then lose a molecule of water by forming another ring. The ketone (I) gives a very good yield of the ethyl derivative (VI) by the action of ethyl iodide in the presence of sodium ethoxide, although, as already mentioned, no trace of the corresponding methyl derivative



(VII) is formed in the presence of sodium methoxide; methylation proceeds readily in a neutral solvent. The alkyl derivatives cannot

be further alkylated and no longer give a colour with ferric chloride or sodium ethoxide. They show a slight exaltation of the molecular refraction comparable with that found in the parent substance (see p. 2129); they are, however, concordant amongst themselves.

Attempts were made to condense the ketone (I) with benzaldehyde and piperonal, but without success.

*cyclo*Pentanone could not be condensed with acetophenone to give the ketone (II); this was, however, prepared in the same way as the higher homologue, from α-Δ^1-*cyclo*pentenyl- and *cyclo*pentylidene-acetyl chlorides (compare Kon and Linstead, *loc. cit.*), the same substance being obtained in each case. The compound resembles the higher homologue in every respect; it gives a similar product on treatment with ozone, condenses with ethyl sodioacetoacetate, and gives an α-ethyl derivative, though in poorer yield. These reactions show that the compound is mobile like the higher homologue.

When the Blaise reaction was applied to the chlorides of diethylacrylic acid and its βγ-isomeride, two *different* ketones (III and IV) were obtained. The αβ-ketone showed a considerable exaltation of the molecular refraction and was characterised by the formation of an *oximino-oxime*. It also condensed with ethyl sodioacetoacetate to give the cylic compound (VIII).

$$\text{(III.)} \longrightarrow \begin{matrix} \text{Et} \\ \text{Et} \end{matrix}\!\!>\!\text{C}\!<\!\begin{matrix} \text{CH}_2\cdot\text{CPh} \\ \text{CH}_2\text{—CO} \end{matrix}\!\!>\!\text{CH} \quad \text{(VIII.)}$$

The ketone (IV) had a normal molecular refraction and did not form an oximino-oxime; when treated with ethyl sodioacetoacetate, it gave the compound (VIII) in about the same yield as its isomeride; it is clear, therefore, that in the presence of sodium ethoxide the βγ-ketone is partly converted into the αβ. The actual equilibrium in the presence of sodium ethoxide was not investigated, because the semicarbazone of the ketone (III) is an extremely intractable substance and the separation of a mixture of the two ketones is practically impossible. The action of 25% sulphuric acid on the αβ-ketone causes conversion into the βγ-isomeride (in addition to some hydrolysis), to the extent of roughly 25% in 4 hours, whilst the βγ-ketone is not affected by this treatment.

The ketones (III) and (IV) are therefore analogous to the pair of ketones investigated by Kon and Linstead, and exhibit retarded mobility in the same way, that is, they can be prepared in a pure state and are stable in the absence of reagents, but form an equilibrium mixture in the presence of sodium ethoxide.

All the ketones here described undergo hydrolytic fission on prolonged boiling with acids or alkalis, being split into acetophenone

and *cyclo*hexanone, *cyclo*pentanone and diethyl ketone, respectively. *cyclo*Hexenylacetone undergoes a similar fission.

This reaction cannot safely be employed as a guide to the structure of a ketone, since both (III) and (IV) give the same products. It is probable that water is first added to the double linking of the ketone, the hydroxyl attaching itself in each case to the β-carbon atom; the hydroxy-ketone can then undergo the reversed aldol reaction (compare J., 1923, **123**, 1717):

$$\left.\begin{array}{l} CEt_2{:}CH{\cdot}COPh + H_2O \\ CHMe{:}CEt{\cdot}CH_2{\cdot}COPh + H_2O \end{array}\right\rangle \rightarrow CEt_2(OH){\cdot}CH_2{\cdot}COPh.$$

EXPERIMENTAL.

α-Δ¹-cyclo*Hexenylacetophenone* (I).

A mixture of 5% sodium ethoxide (1000 c.c.), *cyclo*hexanone (200 g.), and acetophenone (275 g.) was kept ice-cold for a few hours and at room temperature for 3 days; water was then added. The oil produced, isolated and dried in ether, was distilled, the fraction, b. p. 172—178°/14 mm., being almost pure α-Δ¹-cyclo*hexenylacetophenone*; more was obtained by redistillation of the higher fractions, the total yield being about 40% (Found: C, 83·9; H, 8·1. $C_{14}H_{16}O$ requires C, 84·0; H, 8·1%). The ketone is a somewhat viscous, pale yellow oil, $d_4^{21°}$ 1·04157, $n_D^{21·0°}$ 1·55630, $[R_L]_D$ 61·78 (calc., 61·39*); it gives an orange colour with alcoholic ferric chloride. It is not very volatile in steam and therefore the usual method of purification could not be applied.

The *semicarbazone*, prepared by keeping the components in warm methyl-alcoholic solution for an hour, gradually separated as a crystalline cake during 2 days. It crystallised from methyl alcohol in large, transparent, rhombic crystals, m. p. 115—117°, which contained about half a molecule of methyl alcohol; after drying at 100°, the crystals became opaque and melted at 120—121° (Found: C, 70·0; H, 7·4. $C_{15}H_{19}ON_3$ requires C, 70·0; H, 7·4%). This form is obtained direct by crystallisation from dilute methyl alcohol, whilst from benzene a product of indefinite melting point (94—115°) is obtained; only one definite form of the semicarbazone has been isolated up to the present.

The semicarbazone was only slowly decomposed by oxalic acid, but was completely hydrolysed by boiling 5% sulphuric acid in 1

* This and all subsequent theoretical values were calculated from the observed molecular refraction of acetophenone (Auwers and Eisenlohr, *J. pr. Chem.*, 1910, **82**, 65).

hour. The ketone obtained had b. p. 176—178°/17 mm., $d_4^{18\cdot0°}$ 1·04414, $n_D^{18\cdot0°}$ 1·55886, $[R_L]_D$ 61·87.

The *oxime*, prepared in the presence of potassium hydroxide, was an oil which readily solidified on rubbing with petroleum and separated from dilute alcohol in long needles, m. p. 101—102° (Found: C, 78·0; H, 7·8. $C_{14}H_{17}ON$ requires C, 78·1; H, 7·9%).

Oxidation of α-cyclo*Hexenylacetophenone with Ozone.*—The ketone (5 g. at a time) was ozonised in dry chloroform; the ozonide was freed from chloroform under reduced pressure and decomposed by warming with water. The product was a viscous oil with a smell reminiscent of hexahydrobenzaldehyde; it gave a mirror with ammoniacal silver nitrate and a red colour with alcoholic ferric chloride. On distilling it in steam no trace of *cyclo*hexanone was obtained, the only volatile product being benzoic acid. The residue from one experiment was treated with 10% sulphuric acid and again distilled in steam; a further quantity of benzoic acid (total yield 60%) was then obtained together with a little acetophenone, doubtless derived from the hydrolysis of some of the initial material (see p. 2135); no other products could be identified.

Synthesis of α-cyclo*Hexenylacetophenone.*—To a Grignard reagent, prepared from 26 g. of bromobenzene and cooled in ice, was added as rapidly as possible a solution of zinc chloride (1 mol.) in ether (prepared by allowing freshly fused zinc chloride to stand with 2 mols. of dry ether for 24 hours). Dry toluene (250 c.c.) was added and the mixture vigorously shaken; a suspension of the organometallic complex was produced which was freed from ether below 30° under reduced pressure. The suspension was cooled in ice and 13 g. (½ mol.) of α-Δ^1-*cyclo*hexenylacetyl chloride (b. p. 92—93°/17 mm., prepared from the solid acid, m. p. 38°), diluted with toluene, were slowly run in with vigorous agitation. After 1 hour the ketone was isolated in the usual way (see Part I) and purified by fractionation. A small low fraction consisting of diphenyl was obtained, and 11 g. (67%), b. p. 165—180°/17 mm.; the latter gave on redistillation 10 g., b. p. 168—174°/14 mm., $d_4^{18\cdot0°}$ 1·0422, $n_D^{18\cdot0°}$ 1·55870, $[R_L]_D$ 61·84, which readily formed the semicarbazone, m. p. 120—121° after rubbing with ether but without recrystallisation; this was identical in every respect with that previously obtained.

The experiment was repeated starting with the chloride of *cyclo*hexylideneacetic acid (b. p. 104°/13 mm.; the b. p. given by Birch, Kon, and Norris is too high). The ketone (yield about 64%) had b. p. 168—170°/12 mm., $d_4^{20\cdot5°}$ 1·04209, $n_D^{20\cdot5°}$ 1·55710, $[R_L]_D$ 61·80, and readily gave a semicarbazone identical with that of the ketone obtained from the βγ-acid or prepared by direct condensation.

The ketone can also be obtained by the action of magnesium

phenyl bromide on either of the above acid chlorides in ice-cold ether; the yield, however, seldom reaches 30%, the main portion of the product being an oil, b. p. 200—220°/20 mm., probably consisting of a tertiary alcohol.

Alkylation of α-cyclo*Hexenylacetophenone.*—The ketone was methylated in ether as described in Part V (this vol., p. 1792); the new ketone was then isolated in about 50% yield; no trace of unchanged parent substance appeared to be present, but a certain amount of high-boiling by-product was found. The ketone had b. p. 168—170°/15 mm., $d_4^{18\cdot5°}$ 0·99896, $n_D^{18\cdot5°}$ 1·54314, $[R_L]_D$ 66·36 (calc., 66·11). The *semicarbazone* is very sparingly soluble and separates from methyl alcohol in minute plates, m. p. 191—192° (Found : C, 70·7; H, 8·1. $C_{16}H_{21}ON_3$ requires C, 70·8; H, 7·8%).

The ketone (I) was treated with sodium ethoxide and ethyl iodide as described in Part I. The ethylated ketone was isolated in approximately 90% yield and converted into the *semicarbazone*, which was formed very slowly; at the end of 3 weeks a yield of about 60% was obtained, the crude substance melting above 200°. It crystallised from much ethyl alcohol in minute, iridescent plates, m. p. 212° (Found : C, 71·1; H, 8·1; N, 14·7. $C_{17}H_{23}ON_3$ requires C, 71·6; H, 8·1; N, 14·7%). No trace of the semicarbazone of the parent ketone appeared to be present. The ketone regenerated by means of sulphuric acid was almost odourless; it had b. p. 184—185°/19 mm., $d_4^{21·0°}$ 1·01155, $n_D^{21·0°}$ 1·54077, $[R_L]_D$ 70·85 (calc., 70·63).

An attempt was made to synthesise the ethylated ketone by the method of Haworth and Fife (J., 1914, **105**, 1665). Ethyl α-cyano-*cyclo*hexylideneacetate was ethylated, and the new ester kept for 4 hours with sodium ethoxide at 40° without previous purification (compare Birch and Kon, *loc. cit.*). α-cyclo*Hexylidenebutyronitrile* was isolated from the product in 67% yield and had $d_4^{21·0°}$ 0·92283, $n_D^{21·0°}$ 1·48917, $[R_L]_D$ 46·67 (calc., 45·53). Magnesium phenyl bromide in ether had however, no action on the nitrile, which was isolated unchanged.

Action of Ethyl Sodiocyanoacetate.—The ketone was treated on the steam-bath with ethyl cyanoacetate and sodium ethoxide for 6 hours. The product was divided into neutral and acid portions; the neutral portion contained, in addition to unchanged initial material, a considerable quantity of acetophenone, evidently formed as the result of fission; no definite compounds were isolated from the acid fraction, as they were uncrystallisable and could not be distilled.

Action of Ethyl Sodioacetoacetate.—The ketone, ethyl acetoacetate, and alcoholic sodium ethoxide in molecular proportions were heated under reflux or left in the cold; water and a little acid were then added, the oil was taken up in ether and distilled under reduced

pressure, much carbon dioxide being evolved; the low fraction obtained consisted of initial material, whilst the fraction, b. p. 200—240°/20 mm., gave on redistillation a thick oil, b. p. 210—220°/20 mm., which solidified on cooling and formed stout needles, m. p. 69—70°, from dilute alcohol, consisting of the ketone (V) (Found: C, 84·8; H, 8·3. $C_{17}H_{20}O$ requires C, 85·0; H, 8·3%). The best yield of this (about 48%) was obtained when the reaction mixture was kept on the steam-bath for a week, whilst about 25% was obtained in the cold. The compound readily gave a highly insoluble *semicarbazone*, which formed small needles, m. p. 219°, from alcohol; these on exposure to sunlight assumed a bright yellow colour which disappeared on recrystallisation (Found: C, 72·5; H, 7·8; N, 14·4. $C_{18}H_{23}ON_3$ requires C, 72·7; H, 7·8; N, 14·1%).

Action of Sodium Ethoxide.—A mixture of the ketone (I) and alcoholic sodium ethoxide was kept for 4 days at room temperature and was then diluted with water and extracted with much ether. The extract on evaporation deposited a crystalline solid (35% yield) together with a small amount of unchanged ketone, which was removed by means of ether. The solid crystallised from benzene and petroleum in short needles, m. p. 201° (Found: C, 83·8; H, 8·1. *M*, cryoscopic in benzene, 389. $C_{28}H_{32}O_2$ requires C, 84·0; H, 8·1%; *M*, 400). The compound was sparingly soluble in ether, alcohol, or acetone, readily in benzene, ethyl acetate, or chloroform. It dissolved in hot acetic acid, but on diluting and cooling the solution a new compound, crystallising from dilute alcohol in felted needles, m. p. 106°, was precipitated (Found: C, 87·9; H, 7·9. $C_{28}H_{30}O$ requires C, 87·9; H, 7·9%). The compound is very soluble in alcohol and in ether.

Hydrolysis.—The ketone (10 g.) was boiled with an equal weight of potassium hydroxide in 70 c.c. of water for 36 hours; 4·3 g. remained unchanged, whilst *cyclo*hexanone and acetophenone were isolated from the lower-boiling fraction and identified by their semicarbazones. In 96 hours the hydrolysis was practically complete, a 95% yield of acetophenone-semicarbazone being isolated. In addition to a small amount of benzoic acid, a 70% yield of acetophenone was obtained in 24 hours by the agency of methyl-alcoholic potassium hydroxide (12 g. in 10 c.c. of water and 10 c.c. of alcohol). 25% Sulphuric acid (by vol.) produced about 50% fission in 36 hours.

α-Δ^1-cyclo*Pentenylacetophenone* (II).

Attempts to effect the direct condensation of *cyclo*pentanone with acetophenone were fruitless, the only ketone contained in the high fraction of the reaction product being *cyclo*pentylidene*cyclo*pentanone (Wallach, *Ber.*, 1896, **29**, 2963). The new ketone was therefore

prepared synthetically by Blaise's method, exactly as described for the higher homologue, starting with the two pure acids, m. p. 51—52° and 63—64°, respectively (Kon and Linstead, J., 1925, **127**, 616). A 65% yield of the same ketone giving the same semicarbazone was obtained in either case (that prepared from the αβ-acid had b. p. 160—165°/16 mm., $d_4^{18\cdot0°}$ 1·0542, $n_D^{18\cdot0°}$ 1·56740; that from the βγ-acid had b. p. 164—165°/16 mm., $d_4^{18\cdot5°}$ 1·05251, $n_D^{18\cdot5°}$ 1·56637). The *semicarbazone* is less soluble than that of the ketone (I) and forms stellate clusters of needles, m. p. 157°, from methyl alcohol (Found : C, 69·0; H, 7·2. $C_{14}H_{17}ON_3$ requires C, 69·1; H, 7·0%). A second form of the semicarbazone could not be isolated. The *ketone* regenerated from it had b. p. 163—165°/16 mm., $d_4^{20\cdot0°}$ 1·04982, $n_D^{20\cdot0°}$ 1·56437, $[R_L]_D$ 57·69 (calc., 56·77); it gave a deep orange colour with alcoholic ferric chloride.

Oxidation.—The product obtained by treating the ketone with ozone was exactly analogous to that obtained from the higher homologue; a 67% yield of benzoic acid was isolated after hydrolysis of the ozonide with sulphuric acid; no other recognisable product was isolated.

Alkylation.—The ketone was treated with ethyl iodide in the presence of sodium ethoxide as described on p. 2134. About 80% of ethylation product was obtained, the remainder being a high-boiling oil. On treatment with semicarbazide, a crystalline *semicarbazone* formed slowly (yield 37%); it separated from much alcohol in small plates, m. p. 196·5° (Found : C, 70·7; H, 7·8. $C_{16}H_{21}ON_3$ requires C, 70·8; H, 7·8%). The ketone regenerated from it was odourless and had b. p. 162°/11 mm., $d_4^{18\cdot5°}$ 1·01725, $n_D^{18\cdot5°}$ 1·54191, $[R_L]_D$ 66·25 (calc., 65·46).

Action of Ethyl Sodioacetoacetate.—The condensation was carried out as described on p. 2134. The product did not solidify and was therefore isolated in the form of its *semicarbazone*, which was obtained in about 60% yield; the actual yield of condensation product is doubtless higher. The semicarbazone separates from alcohol in small prisms, m. p. 193°, and turns yellow on exposure to light (Found : C, 72·2; H, 7·8. $C_{17}H_{21}ON_3$ requires C, 72·0; H, 7·5%).

Action of Sodium Ethoxide.—The reaction was complete after 48 hours in the cold; the product was, however, an uncrystallisable gum.

Hydrolysis.—This was carried out by means of aqueous potassium hydroxide; a yield of 50% of acetophenone was obtained after 36 hours' boiling.

α-Phenyl-γ-ethyl-Δ$^{\beta}$-penten-α-one (III).

Diethyl ketone could not be condensed with acetophenone. The ketone was therefore prepared by the Blaise reaction from the

chloride of ββ-diethylacrylic acid, obtained as described by Kon and Linstead (*loc. cit.*); the acid had b. p. 117—119°/14 mm., $d_4^{20\cdot0°}$ 0·9693, $n_D^{20°}$ 1·46539, $[R_L]_D$ 36·56. The yield of ketone was nearly 80%; it had b. p. 146—148°/13 mm., $d_4^{21\cdot6°}$ 0·98716, $n_D^{21\cdot6}$ 1·54372, $[R_L]_D$ 60·14 (calc., 58·96). The *semicarbazone* was not easily formed and remained oily for several weeks; eventually a very small amount of solid was isolated which melted, after repeated crystallisation from methyl alcohol, at 90° (Found: C, 68·7; H, 8·0. $C_{14}H_{19}ON_3$ requires C, 68·5; H, 7·8%). The oily semicarbazone was purified by distillation in steam, after which oxalic acid was added and the distillation repeated; the pure *ketone* so obtained had b. p. 138°/8 mm., $d_4^{18\cdot0°}$ 0·98638, $n_D^{18\cdot0°}$ 1·54353, $[R_L]_D$ 60·10.

Oxime.—The ketone was heated for 4 hours with hydroxylamine hydrochloride (2 mols.) and potassium hydroxide in alcoholic solution. The *oximino-oxime* so obtained crystallised from benzene and petroleum in short needles, m. p. 158° (Found: C, 66·2; H, 8·7. $C_{13}H_{20}O_2N_2$ requires C, 66·0; H, 8·5%). If only one molecule of the reagent was used and the mixture kept in the cold for 24 hours, the *compound* obtained on dilution consisted of fine needles, m. p. 101—102° after crystallisation from petroleum (Found: C, 70·7; H, 8·7. $C_{13}H_{19}O_2N$ requires C, 70·5; H, 8·7%). It has the composition of the monoxime plus one molecule of water and is probably formed by the addition of hydroxylamine to the double bond of the ketone.

Hydrolysis.—The action of aqueous potassium hydroxide for 36 hours led to the formation of 45% of acetophenone; in addition, a high fraction (about 40%) was obtained which did not consist of the unchanged ketone but of the βγ-isomeride (IV, see below), which was identified by its semicarbazone. The ketone (III) was also boiled with 25% sulphuric acid for 4 hours; the high-boiling fraction obtained was a mixture of the initial material with the βγ-isomeride; judging from the optical properties ($[R_L]_D$), about 30% conversion had taken place, but it is difficult to estimate this. A small amount of the βγ-semicarbazone was isolated from the mixture.

Action of Ethyl Sodioacetoacetate.—The condensation was carried out as before, the mixture being heated for 48 hours, then left in the cold for 24 hours. About one-third of the ketone was recovered, and this appeared to have undergone partial conversion to the βγ-ketone. The high-boiling fraction did not solidify, but a *semicarbazone*, crystallising from alcohol in rosettes of needles, m. p. 178—179°, was obtained from it. It was identical with that obtained from the βγ-ketone (*q.v.*).

α-Phenyl-γ-ethyl-Δ$^{\gamma}$-penten-α-one (IV).

This ketone was obtained, in 83% yield, exactly like its αβ-isomeride from the chloride of γ-ethyl-Δ$^{\gamma}$-pentenoic acid (Kon and Linstead, *loc. cit.*). The latter was prepared by boiling β-hydroxy-ββ-diethylpropionic acid with dilute sulphuric acid (1 : 4) for 1½ hours; when freed from a small quantity of lactone, it had b. p. 113—115°/13 mm., $d_{4^\circ}^{20\cdot0^\circ}$ 0·96597, $n_{D}^{20\cdot0^\circ}$ 1·45113, $[R_L]_D$ 35·71. The yield was only 40%, but the product was more easily obtained pure than by the process originally used.* The ketone prepared from it had b. p. 135—136°/10 mm., $d_{4^\circ}^{18\cdot0^\circ}$ 0·98945, $n_{D}^{18\cdot0^\circ}$ 1·53679, $[R_L]_D$59·33 (calc., 58·96). The *semicarbazone* separated from ethyl acetate in small plates, m. p. 171° (Found: C, 68·4; H, 7·9. $C_{14}H_{19}ON_3$ requires C, 68·5; H, 7·8%). The *ketone* regenerated from it had b. p. 146°/17 mm., $d_{4^\circ}^{19\cdot5^\circ}$ 0·98513, $n_{D}^{19\cdot5^\circ}$ 1·53372, $[R_L]_D$ 59·34. A crystalline oxime was not obtained.

Hydrolysis.—The ketone was boiled with aqueous potassium hydroxide for 36 hours. Diethyl ketone was identified in the product by its *p*-nitrophenylhydrazone, m. p. 138°; about 60% of acetophenonesemicarbazone was also obtained, whilst the high fraction (about 20%) consisted of initial material. The hydrolysis was also carried out with dilute sulphuric acid; two-thirds of the ketone remained unattacked, and this was the βγ-ketone, no conversion into the isomeride having taken place. It is therefore clear that only the αβ-ketone (III) is isomerised by boiling with sulphuric acid.

Action of Ethyl Sodioacetoacetate.—The condensation proceeds precisely as in the case of the αβ-ketone, the same yield of condensation product being obtained. It was identified by means of the semicarbazone, m. p. 178—179° (Found: C, 71·7; H, 8·0. Calc.: C, 71·6; H, 8·1%).

Hydrolysis of Δ^{1}-cyclo*Hexenylacetone.*—The ketone was boiled with aqueous potassium hydroxide for 36 hours. The product gave a low fraction in which acetone could be identified; *cyclo*hexanone was separated in the form of its semicarbazone, the yield being about 60%. The remainder consisted of the unchanged ketone with a quantity of gummy impurity.

The authors' thanks are due to the Royal Society and the Chemical Society for grants which have defrayed the expenses of this investigation.

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* We are indebted to Dr. R. P. Linstead for this method of preparation.

CCLXXXIII.—*The Propagation of Flame in Mixtures of Methane and Air. Part IV. The Effect of Restrictions in the Path of the Flame.*

By William Ronald Chapman and Richard Vernon Wheeler.

In earlier parts of this research (J., 1920, **117**, 36, 1227) preliminary references were made to the high speeds attained by the flame during explosions of methane and air in a tube the diameter of which was restricted at several points. For example, it was recorded (*loc. cit.*, p. 47) that in a steel tube 30·5 cm. in diameter and 90 m. long, open at both ends, in which restrictions (consisting of thin steel rings which reduced the diameter of the tube to 28·6 cm.) were introduced at two points, the development of the detonation-wave, or some mode of combustion of similar intensity, seemed imminent. This effect of the restrictions was tentatively assumed to be one of turbulence, caused by currents induced locally as the flame passed through the restrictions. A similar explanation, an effect of turbulence, was held to account for the much greater speed at which flame travels in a given mixture of methane and air, when that mixture is passed through a tube as a current, than it does when the mixture is initially at rest within the tube.

The research has developed along two lines: (1) A study of the effect on flame speed of an artificial movement given to the inflammable mixture; and (2) a study of the propagation of flame, in an initially quiescent mixture, along a tube containing restrictions. The former is still in progress and will be described at a later date. The present paper deals with the effect of restrictions as studied mainly by experiments on a small scale in the laboratory, supplemented by tests on a larger scale. The main object of the work has been to determine the maximum speed at which flame can travel in mixtures of methane and air, initially at rest and at atmospheric temperature and pressure.

The laboratory experiments were carried out in a brass tube 5 cm. in diameter and 240 cm. long, built up of short sections bolted together. The restrictions used were brass annuli, usually 1 mm. in thickness, which could be introduced at given points along the tube between the sections. Certain sections of the tube were provided with a longitudinal window of quartz, 4 mm. wide, through which the movements of the flame could be photographed, through a quartz lens, on a rapidly revolving film. The tube was mounted horizontally and was fully open at both ends when the explosions were produced, the mixture being ignited at one end. In all the series of experiments described in this paper, mixtures of methane

and air containing between 9·5 and 10·0% of methane, in which the speed of flame normally is fastest, were used.

The Propagation of Flame in an Unrestricted Tube.

In order that the effects of restrictions could be appreciated it was necessary to repeat the experiments on the propagation of flame in an unrestricted tube open at both ends made by Mason and Wheeler (J., 1920, **117**, 36). The results differed slightly * from those obtained by Mason and Wheeler and a description of them is necessary. The flame accelerated gradually over the first 80 cm. and then was slightly retarded, faint undulations of the flame front making their appearance. These undulations became more marked and eventually the flame assumed a definitely vibratory character over a distance of about 15 cm., during which its mean forward speed increased. The speed of the flame continued to increase after the vibrations had died away until the end of the tube was reached. The periodicity of the vibrations was that of the fundamental tone of the tube, namely 98. A photograph of the flame throughout its passage along the tube, is reproduced in Fig. 1, Plate I. The full length of the tube is shown in the photograph which is composite, being obtained by joining together photographs of successive sections taken in separate experiments. The flame travelled from left to right and the photographic film can be regarded as moving vertically upwards. Its speed of travel was 73 cm. per sec. Since the photograph has been reduced in size to about one-fifth, the speed of travel of the film in the reproduction can be regarded as about 14 cm. per sec. This applies also to the other photographs on Plate I. The chief difference between this photograph and that obtained by Mason and Wheeler (an important one from the point of view of the present research) lies in the absence of intense vibrations.

The Effect of One Restriction.

A number of trials were made to determine with what reduction in diameter of the tube, and at what position along it, the maximum effect would be obtained.

The Amount of Restriction.—A ring of brass, 1 mm. in thickness,

* The differences were due to the fact that a flame held at the mouth of the tube, instead of an electric spark a few cm. within the tube, as in Mason and Wheeler's experiments, was used to ignite the mixtures. As explained in a previous paper (J., 1919, **115**, 578), the mechanical disturbance caused by the electric spark induces marked vibrations of the flame. In the present experiments, it was necessary to prevent the occurrence of such vibrations as far as possible.

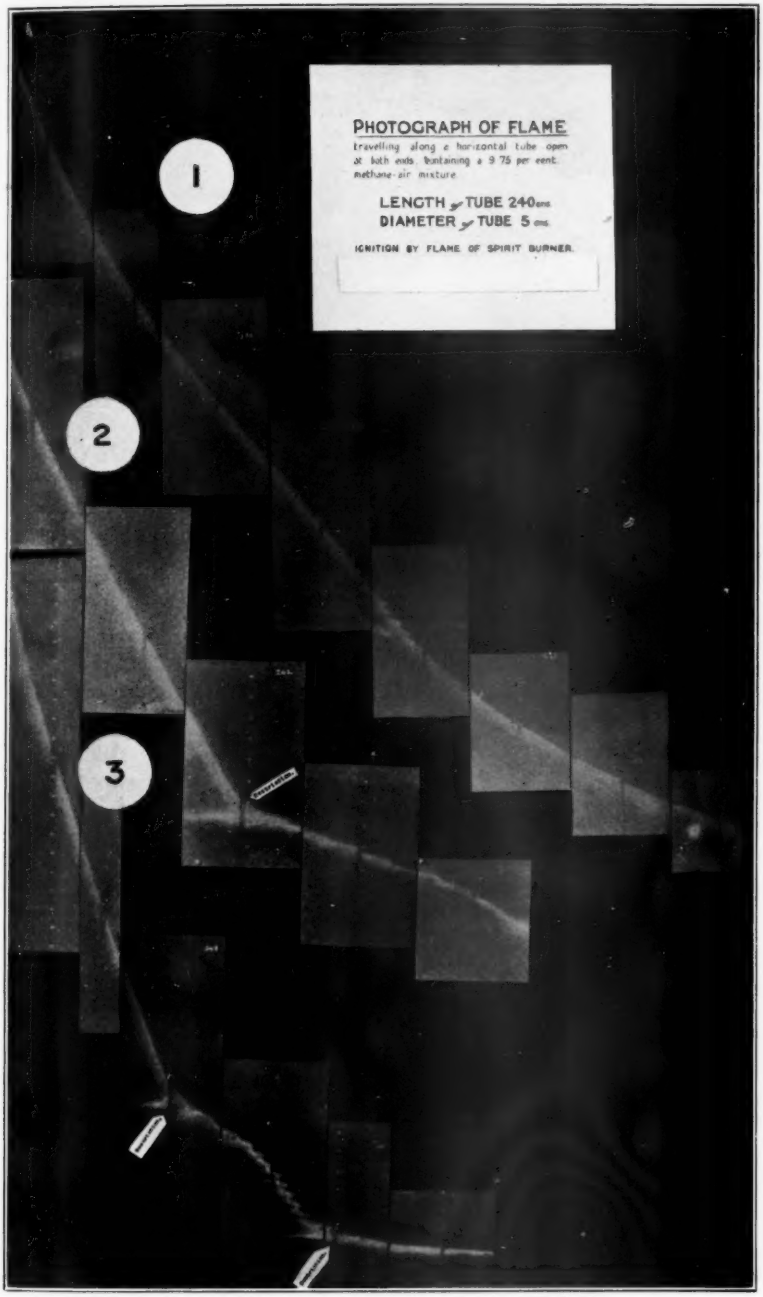
PHOTOGRAPH OF FLAME
travelling along a horizontal tube open at both ends, containing a 9·75 per cent. methane-air mixture.
LENGTH of TUBE 240 cms.
DIAMETER of TUBE 5 cms.
IGNITION BY FLAME OF SPIRIT BURNER.
1
2
3

FIG. 1.—*Unrestricted tube.* FIG. 2.—*One restriction, reducing the diameter of the tube to 2·5 cm., at a point 80 cm. from point of ignition.* FIG. 3.—*Two restrictions, 60 and 110 cm. from point of ignition.*

[*To face p.* 2140.]

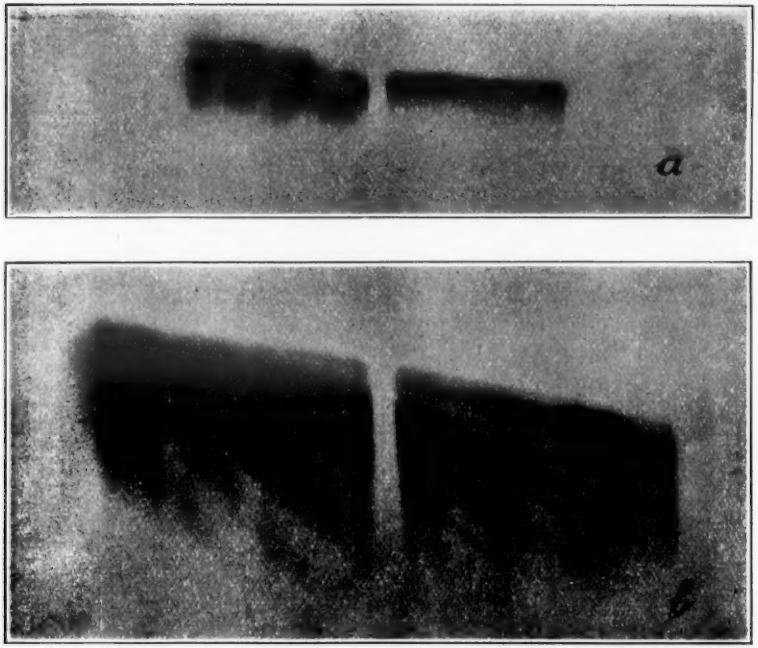

FIG. 1.

(a) *Flame passing through the last six of a series of twelve restrictions, 5 cm. apart (left half of photograph).*

(b) *Flame travelling at uniform high speed (420 m. per sec.) after passing through twelve restrictions, 5 cm. apart.*

FIG. 2.—*The movements of flame at a restriction.*

PLATE II.

was inserted at a point, somewhat arbitrarily chosen, 40 cm. from the end of the tube at which ignition of the mixture was to be effected. In successive experiments, rings with holes 3·6, 2·5, and 1·5 cm., respectively, in diameter were used, so that the effect of an increasing amount of restriction to the passage of the flame along the tube could be determined.

The mean speeds of the flames over successive intervals of 5 or 10 cm., up to and for a short distance beyond the restriction, are recorded in Table I. For comparison, the speeds obtained when an unrestricted tube was used are also recorded.

TABLE I.

The Effect of the Amount of Restriction.

Mean Speed of Flame (cm. per sec.).

Distance from point of ignition (at one end of the tube).	Unrestricted tube.	Restrictions 40 cm. from point of ignition.		
		3·6 cm. diam. hole.	2·5 cm. diam. hole.	1·5 cm. diam. hole.
5—15	106	98	98	93
15—25	134	122	118	94
25—30	146	138	121	95
30—35	158	147	124	95
35—40	170	147	124	95
		(Restriction inserted here)		
40—45	182	256	341	249
45—55	194	156	475	
55—65	206	230	600	

It will be seen that in each instance the speed of the flame was retarded before the restriction was reached, and was enhanced after the restriction had been passed, the greatest increase being produced when the restricting ring reduced the diameter of the tube by one-half. It will be noticed, also, that the speed of the flame as it travelled between the point of ignition and the restriction tended to become uniform, the tendency being more marked the greater the amount of restriction.

The Position of the Restriction.—Using the restricting ring that had been found to produce the optimum effect, *viz.*, that with a hole 2·5 cm. in diameter, a series of experiments was made in which the position of this ring along the tube was varied. The results are recorded in Table II.

The general effects of the restriction on the speed of the flame, a retardation as the ring was approached and an acceleration after it had been passed, were the same whatever its position along the tube, but the intensity of the effects increased the further the restriction was removed from the point of ignition.

TABLE II.

The Effect of the Position of the Restriction.

Mean Speed of Flame (*cm. per sec.*).

Distance from point of ignition (at one end of tube).	Unrestricted tube.	Restricted tube, aperture 2·5 cm. Distance from point of ignition. 40 cm.	80 cm.	105 cm.
5—15	106	98	96	103
15—25	134	118	129	135
25—35	152	123	142	143
35—40	170	124 (Restriction)	151	147
40—45	182	341	157	150
45—55	194	475	164	152
55—65	206	600	165	155
65—75	240	640	164	158
75—80	254	936	164 (Restriction)	158
80— 85	254	936	424	158
85— 95	249	779	1050	93
95—105	231	647	895	70 (Restriction)
105—110	220	650	880	2780
110—115	220	650	880	7500
115—125	237	650	705	7500
125—135	285	725	628	2430
135—145	350	420	803	3150

The Thickness of the Restriction.—Experiments were made in which the thickness of a restricting ring, having a hole 2·5 cm. in diameter and placed 80 cm. from the point of ignition, was varied between 1 and 20 mm. The effect of this variation was slight: the thinnest ring caused the greatest increase in speed of the flame, as the results recorded in Table III show.

TABLE III.

The Effect of the Thickness of the Restriction.

Mean Speed of Flame (*cm. per sec.*).

Mean speed of flame.	Thickness of restriction. 1 mm.	10 mm.	20 mm.
Over 20 cm. before restriction	164	160	157
Over 5 cm. beyond restriction	424	395	380

From these results it was considered that the most marked effect on the speed of the flame would be produced, under the conditions of the experiments, if the restricting rings were 1 mm. in thickness with a hole 2·5 cm. in diameter. Such rings were used throughout the remainder of the experiments described in this paper. Fig. 2, Plate I, illustrates a typical experiment with one such restricting ring 80 cm. from the point of ignition. The speed of travel of the

photographic film in this experiment was 70 cm. per sec. The movement of the flame over the first 155 cm. only is shown in this photograph.

The Effect of Two Restrictions.

The effect of placing two restricting rings in the path of the flame is illustrated by the results recorded in Table IV.

TABLE IV.

The Effect of Two Restrictions.

Mean Speed of Flame (cm. per sec.).

Mean speed of flame.	Distance from point of ignition (at one end of tube).		
{First restriction / Second „	40 cm. / 110 cm.	60 cm. / 110 cm.	80 cm. / 110 cm.
Over 10 cm. before first restriction	142	120	115
Over 10 cm. beyond first restriction	282	315	480
Between the two restrictions	240	255	360
Over 10 cm. before second restriction	229	240	265
Over 10 cm. beyond second restriction	3070	3680	3875

The manner of movement of the flame in the vicinity of each restriction was similar and comparable with that obtaining when only one was present. Thus, the speed of the flame, which had increased after passing through the first restriction, decreased as it approached the second, to increase again after passing through it. A typical photograph of the flame as it travelled through the first 155 cm. of the tube is illustrated in Fig. 3, Plate I. The speed of travel of the film in this experiment was 68 cm. per sec. Since for each of the photographs reproduced on Plate I the speed of travel of the film was nearly the same, direct comparison of the speeds of the flames is possible.

The Effect of Three or More Restrictions.

The sequence of events was the same at each restriction as their number was increased, provided that they were sufficiently far apart. Thus, when there were three, placed 40, 70, and 110 cm., respectively, from the point of ignition, the mean speeds of the flame over measured lengths of the tube were as follows :

Distance from point of ignition (cm.).	Mean speed of flame (cm. per sec.).	Distance from point of ignition (cm.).	Mean speed of flame (cm. per sec.).
5—15	100	(Restriction)	
15—25	114	75— 85	3,351
25—35	123	85—105	2,310
(Restriction)		(Restriction)	
45—55	491	115—135	22,500
55—65	468		

If the restrictions were placed closer together, *viz.*, 5 cm. apart, as was done in several series of experiments, there was no appreciable retardation of the speed of the flame travelling between any two of them, but a greatly enhanced speed was attained after passing each. It seemed possible, therefore, that, by introducing a sufficient number of restrictions, speeds comparable with that of the detonation-wave might be attained. Their number was accordingly increased by stages up to 20, with a distance of 5 cm. between each.

The highest speed of flame, 420 m. per sec., was obtained when 12 restrictions were present, an increase in the number effecting no change. This speed, once acquired, was maintained constant throughout the remainder of the tube. The length of the tube was varied between 2 and 3 m., and the position of the first of the set of restrictions relative to the point of ignition was varied between 1/5 and 2/5 of the length of the tube. Under all conditions, the same speed of flame, 420 m. per sec., was obtained. The quartz windows, and windows of thick plate glass used subsequently, were shattered to powder in each experiment. The flame had a much higher actinic value than that of the normal flame in methane–air mixtures, yielding a dense black image when photographed through plate glass on a film moving at a speed of 9 m. per sec. (time of exposure, 1/2000 sec.). The normal flame in methane–air mixtures produces no image when photographed under such conditions. Fig. 1, Plate II, illustrates (*a*) the appearance of the flame as it passed through some of the restricting rings, and (*b*) its uniform high speed subsequently.

Speeds of flame of the same magnitude were measured during experiments in an iron tube 30·5 cm. in diameter and 100 m. long, open at both ends, with restricting rings reducing the diameter to 10 cm. at two points 11·4 m. apart, the first being 22 m. from the end of the tube at which ignition was effected. The maximum speed of flame in the same tube without restrictions was 10 m. per sec. In these large scale experiments continuous records of pressure were obtained at several points close to the restrictions. The maximum pressure recorded, which was always obtained just beyond the last restriction, was 3·9 atm., whilst no appreciable pressure could be measured before the flame reached the first restriction.

The detonation-wave cannot be set up in methane–air mixtures initially at atmospheric pressure, and the speed attained by the flame in the present experiments with 12 restrictions in a 2·5 cm. diameter tube falls far short of the lowest at which a true detonation-wave has been measured in mixtures of methane, oxygen, and nitro-

gen, *viz.*, 1,150 m. per sec.* The marked actinic power of the flame, however, together with the fact that a high pressure must have been developed to shatter the plate-glass windows so completely, suggests that a mode of translation of the flame in a methane–air mixture approximating to that existing during the detonation-wave was established, temporarily, in and beyond the restricted portion of the tube.

An Explanation of the Effects Produced by Restrictions.

In every photograph of the flame as it passes through a restriction, it has been observed (1) that there is a slight acceleration of speed over a distance of 2 or 3 cm. before the restriction is reached, and (2) that, just as the flame-front has passed through the restricting ring, a secondary flame moves back rapidly, over a distance of 5 to 30 cm., towards the point of ignition. These effects are illustrated in Fig. 2 on Plate II. This is a reproduction (actual size) of a photograph of the flame as it travels over a distance of 15 cm. on either side of a restriction. The speed of travel of the film in this experiment was 66 cm. per sec.

Apart from these two local effects, the general effects of a restriction on the propagation of flame along a tube are, as already noted, to decrease the mean speed before and to increase the mean speed beyond the restriction.

The explanation originally advanced (*loc. cit.*), that the enhanced speed acquired by the flame after it has passed a restriction is due to the creation of turbulence at the restriction, is incomplete. It does not account directly for the maintenance of a high speed of flame over a considerable distance beyond the restriction. An explanation is also required for the fact that the speed of the flame is lower than normal throughout the tube before the restriction is reached, and is slightly accelerated just as it is approached. Consideration of the behaviour of the unburnt gas mixture in the tube ahead of the flame provides an explanation.

A sensitive jet of flame was caused to burn vertically in line with the explosion tube a short distance from the end to which the explosion would travel, and the movements of this flame while the explosion was being propagated were photographed by means of a high-speed cinematograph camera. The photographs showed that, throughout the propagation of the explosion, the flame-jet

* Berthelot (*Compt. rend.*, 1882, **95**, 151) records this speed for the detonation-wave in the mixture $CH_4+4O+8N$. Dixon (*Phil. Trans.*, 1893, *A*, **184**, 97) found that in the mixture $CH_4+3O+5N$ the speed of the detonation-wave was 1,880 m. per sec., and he records that in this mixture the wave was not always established.

outside the tube was deflected in the same direction as that of the flame moving within the tube, the amount of deflection being greater the greater the speed of the explosion. The incidence of a vibratory stage of the explosion was also indicated by the movements of this flame-jet, as were the changes in speed that occurred when restrictions were inserted in the explosion tube.

It can be concluded that, during the propagation of flame in a tube open at both ends, the unburnt mixture in advance of the flame-front is travelling as a current in the same direction as that of the flame, which is therefore travelling in a medium that is itself in motion. The general effects of a restriction in the tube on the speed with which flame travels from point to point along it can be explained as being effects on the speed of the medium in which the flame is moving.

The sequence of events is as follows. When a restriction such as those used in these experiments is ahead of the flame, the resistance offered by it to the movement of the unburnt mixture causes the current, and therefore also the flame, to move more slowly. Just as the restricting ring is approached, the convergence of lines of flow of the mixture causes a slight acceleration of the current, and thus of the flame (Fig. 2, Plate II). The flame passes through the restricting ring as a thin tongue and spreads laterally, so that just beyond the restriction the burning " layer " of mixture suddenly becomes considerably thicker than the normal and there is an abnormal amount of the mixture burnt locally. There is, in consequence, an enhanced speed now given to the current of unburnt mixture ahead of the flame, whilst part of the burning gas is forced back through the restriction (Fig. 2, Plate II). Thereafter, the flame moves, relatively to the walls of the tube, more rapidly because the current of mixture in which it propagates is moving more rapidly.

The effects on the behaviour of the flame, previously described, of successive restrictions spaced widely apart in its path, can be explained in a similar manner as being due to the motion of the medium in which the flame is travelling. When the restricting rings are close enough together, however, the tongue of flame that darts forward at the first restricting ring shoots right through the second and enflames the mixture beyond it whilst the portion between the two is still burning. Combustion thus spreads rapidly throughout a comparatively large volume of mixture, with the result that there is a proportionately rapid movement of the unburnt mixture ahead. By providing a sufficiently large number of restricting rings, spaced not too far apart, the volume of mixture through which this almost simultaneous combustion is induced can be augmented considerably. With the particular diameter of tube

and of restricting ring employed in these experiments, a limit to the volume of mixture that can be suddenly inflamed in this manner appears to have been reached with twelve restricting rings.

Experimental.

The apparatus used in our experiments for obtaining photographic records of the movements of the flames did not differ materially from that described by Mason (J., 1923, **123**, 210). For the insertion of the restricting rings in the brass tube, a groove 0·5 mm. in depth was cut at each flange of the sections that built up the full length of the tube. A restricting ring fitted closely into the recess thus formed at any junction of two sections, whilst the recesses at junctions where a restriction was not desired were filled by brass rings 1 mm. in thickness of the same bore as that of the tube.

The majority of the photographs were taken on Eastman Kodak films, but for some (*e.g.*, those reproduced in Fig. 1, Plate II) Lumière paper was employed. Each photograph of a section of the tube was mounted on a black background in its correct position relative to the remainder. The composite photograph thus obtained measured about 2 feet square. For the experiments made to study the movements of the currents of mixture ahead of the flames, wherein a sensitive jet of flame was photographed, a Debrie cinematograph camera, capable of recording 250 images per second, was employed. The jet of flame was rendered highly actinic by coloration with copper salts.

The mixtures of methane and air were prepared in gas-holders over glycerol and water and were analysed before use. The tube was filled by displacing the air with 6 to 8 times its volume of the mixture, the ends being temporarily closed by brass discs having central tubulures. These discs could be slid away from the ends without causing disturbance of the mixture within the tube. Ignition of the mixture was effected in each instance by the flame of a spirit burner passed slowly across the mouth of the tube.

These experiments form part of a research that we are carrying out for the Safety in Mines Research Board, to whom our thanks are due for permission to publish this paper.

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[*Received, June 15th,* 1926.]

CCLXXXIV.—*The Catalytic Dissociation of Carbon Monoxide.*

By JOHN CLEMINSON and HENRY VINCENT AIRD BRISCOE.

IN 1863, St. C. Deville, experimenting with his "tube chaud et froid," discovered the reversibility of the reaction $CO_2 + C \rightleftharpoons 2CO$ (*Compt. rend.*, 1864, **59**, 873). It was known that heated carbon reduces carbon dioxide to the monoxide, and he observed that when carbon monoxide was heated to about 960° a little carbon dioxide was formed, but above 1000° none could be detected. This is in accordance with general principles, as in the exothermic reaction $2CO \longrightarrow CO_2 + C$ the equilibrium proportion of carbon monoxide would be expected to increase with the temperature. It was early noted (Bell, J., 1869, **22**, 203) that the decomposition is accelerated by the presence of finely-divided metals, such as nickel, cobalt, and iron. This result was further verified by Schenck and his co-workers (*Ber.*, 1903, **36**, 1232, 3663; 1905, **38**, 2139), who found, however, that the oxides of nickel, cobalt, and iron do not increase the velocity of the reaction. Iron, nickel, and cobalt were used as catalytic agents by Boudouard (*Ann. Chim.*, 1901, **24**, 1; *Bull. Soc. chim.*, 1901, **25**, 282, 484) at temperatures of 650°, 800°, and 925°. He found that in presence of these same metals as catalysts the dissociation of carbon monoxide is complete at 445°. Schenck (*loc. cit.*) gave 52·8% as the equilibrium value for this temperature, but it is known that different forms of carbon give widely different values for the equilibrium constant, and this may be the reason for the discrepancy between the results of Boudouard and Schenck.

A table giving the percentage of carbon monoxide in the equilibrium mixture with carbon dioxide in presence of carbon over a range of temperature from 700° to 1200° according to several observers is given by Mellor ("Treatise on Inorganic and Theoretical Chemistry," V, p. 818).

From the foregoing account of the literature, it is apparent that the reaction whereby carbon monoxide yields carbon dioxide and carbon has been fairly thoroughly studied at high temperatures, but it seems to have escaped observation that the same reaction occurs at much lower temperatures.

Preliminary experiments of a qualitative but rigorous nature showed that, whilst pure carbon monoxide in contact with glass and mercury only did not exhibit any shrinkage in volume when kept at 300° for 6 months, the presence of carbon or alumina as catalyst, even at temperatures below 300°, caused carbon mon-

oxide to show a steady contraction in volume which could only be attributed to the reaction $2CO \longrightarrow CO_2 + C$.

The work here described was therefore undertaken to obtain quantitative data as to the rate of the reaction and the final position of equilibrium at relatively low temperatures in presence of a catalyst.

Experimental.

The first series of experiments was directed to ascertaining approximately the minimum temperatures at which carbon, magnesia, and alumina separately as catalysts caused appreciable formation of carbon dioxide in carbon monoxide. The apparatus used enabled carbon monoxide, prepared by dehydration of formic acid and stored over water, to be passed successively through (1) two wash-bottles containing concentrated aqueous potassium hydroxide, (2) two towers containing solid potassium hydroxide, (3) a glass U-tube immersed in an oil-bath which could be maintained at any desired temperature up to 400°, and (4) a wash-bottle fitted with a tap-funnel containing baryta water and provided with a guard-tube, so that clear baryta water could be run into the wash-bottle when it was desired to test for carbon dioxide in the gas issuing from the U-tube. The outlet of (4) communicated with a manometer and a water pump.

In each experiment the whole apparatus beyond the carbon monoxide reservoir was evacuated and then filled with carbon monoxide, and the procedure was repeated four times in succession to ensure the removal of foreign gases. Then, the gas current being maintained at a steady rate, the U-tube was heated to the desired temperature and the baryta water was run into the wash-bottle (4).

The carbon used as a catalyst was sugar-charcoal purified by heating first in chlorine and then in dry hydrogen. Magnesia was prepared by heating magnesium in a stream of oxygen. The alumina was a sample specially prepared for use as a catalyst by Messrs. Peter Spence and Co., Ltd., of Manchester. Before use, the catalysts were heated strongly and cooled in the desiccator.

In a preliminary experiment, the U-tube, containing no catalyst, was maintained at 400° for 4 hours; during the whole of this time the baryta water in (4) remained clear. This affords strong evidence that the reaction $2CO \longrightarrow CO_2 + C$ does not take place at or below 400° when carbon monoxide is in contact with glass surfaces only.

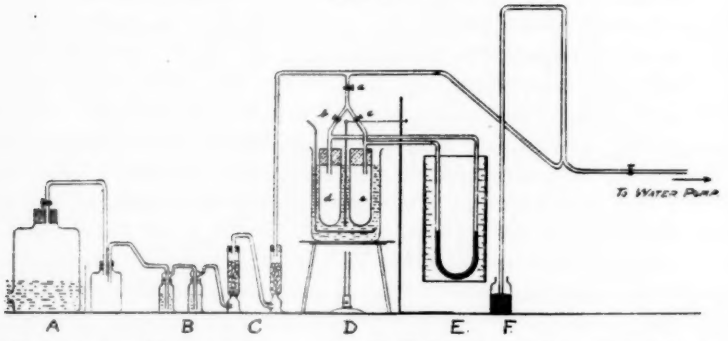
In succeeding experiments with the several catalysts, runs of an hour's duration were made at different temperatures until clear evidence was obtained as to the minimum temperatures at which reaction occurred. These temperatures were: with carbon, 300°;

with magnesium oxide, 290°; and with alumina, 250°. In the last case there were slight signs of the production of carbon dioxide at 215°, but the detection was not definite below 250°.

Making use of the fact that the diminution of volume resulting from the reaction $2CO \longrightarrow CO_2 + C$ is a measure of the extent to which the reaction has occurred, the next series of experiments was designed to ascertain the rate and extent of reaction (1) in the absence of a catalyst, and in the presence of (2) carbon as a catalyst, and (3) alumina as a catalyst.

The apparatus shown in Fig. 1 was attached to the carbon monoxide supply. Taps *a*, *b*, and *c* being open, the whole apparatus was exhausted by means of the water-pump and then filled with

FIG. 1.



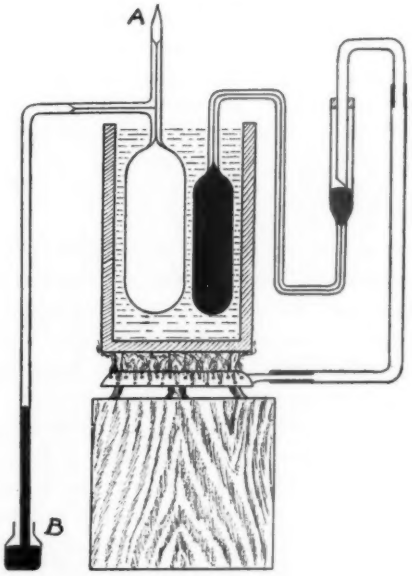
A *Carbon monoxide reservoir.*
B *Aqueous potassium hydroxide.*
C *Solid potassium hydroxide.*
D *Bulbs for carbon monoxide and catalyst.*
E *Mercury gauge.*
F *Manometer.*

carbon monoxide, and by repeating this process of exhausting and filling four times, any residual air was so far removed as to have an inappreciable effect on the observations. The vessels *d* and *e* were surrounded by an oil-bath which was slowly heated and constantly stirred. A blank test confirmed the previous observation that no change in the volume of the gas took place. The U-tube, *e*, was partly filled with mercury, and behind this was placed a millimetre scale so that any rise or fall in the level of the mercury could be measured, and thus any difference of pressure between *d* and *e* observed. During the experiment the taps *b* and *c* were closed, thus isolating the vessels *d* and *e*. The carbon monoxide in the system was initially at a pressure of about 570 mm. Several experiments which need not be detailed agreed in giving definite evidence that with alumina or carbon as a catalyst a definite and considerable diminution of pressure occurred at temperatures below

300°. The presence of traces of carbon dioxide was proved after each experiment by exhausting the bulbs through a little baryta water.

An attempt was next made to measure the rate of change in pressure that may take place when carbon monoxide is heated with a catalyst, say carbon or alumina, at a constant temperature. For this purpose, as the experiments would necessarily extend over considerable periods, an apparatus entirely of glass in one piece was employed. A bulb of Durosil of about 250 c.c. capacity (Fig. 2) was used and about 2 g. of the catalyst were introduced

FIG. 2.



into the bulb through the capillary tube A. To accomplish this, a tap-funnel was attached to A by means of pressure tubing, and the end B was connected to a water-pump through drying tubes containing potassium hydroxide. By closing the tap of the funnel and starting the pump, a partial vacuum was created in the bulb, then, by closing the end B of the tube and opening the tap of the funnel, the finely-divided catalyst, suspended in pure dry ether contained in the funnel, was washed into the exhausted bulb. The process was repeated until the desired quantity of the catalyst had been introduced. The bulb was placed in a bath of hot water until all the ether had evaporated, and as it was imperative that all traces of vapour should be removed a continuous stream of

warm, dry air was afterwards drawn through the bulb for about 8 hours. The apparatus was then connected to the carbon monoxide supply by way of a T-piece attached to A, and was exhausted with the end B dipping under the mercury.

During this process the long arm of the bulb served as a manometer, thus enabling the residual pressure in the bulb to be ascertained. The process of exhausting and filling was repeated four times, the apparatus being filled after each exhaustion with pure carbon monoxide. A simple calculation shows that, the barometric pressure being 736 mm., this procedure should reduce the residual air present after the first evacuation (to 8 mm.) to about 1 part in 7×10^7 parts, whence, making all due allowance for adsorption and other circumstances tending to retain air in the apparatus, it seems safe to conclude that the amount of residual air must be too small to have an appreciable effect on the observations. The first run was carried out at a constant temperature of 250°. A trial run with the bulb before the catalyst was introduced showed that the Durosil glass did not act as a catalyst, no contraction being observed. Such a blank test was carried out with each bulb used subsequently.

In determining the quantity of carbon monoxide present in the bulb for each experiment, the aim was to have the pressure exerted by the gas in the bulb as nearly as possible equal to atmospheric pressure when at the constant temperature at which it was decided to work. This having been achieved, the bulb was sealed off at the top (A) and removed, having its long arm (B) in the mercury reservoir. The bulb was next placed in a bath as shown in Fig. 2.

Paraffin " molle " was used in the bath and the constant temperature maintained by a modified form of mercury thermo-regulator indicated in the figure. This design of regulator was adopted because (1) the feed-tube, being outside the bath, was easily adjusted to the required constant temperature, and (2) fluctuations in temperature, due to the evaporation of the mercury, were minimised, as a proportion of the mercury was at a much lower temperature than that of the bath.

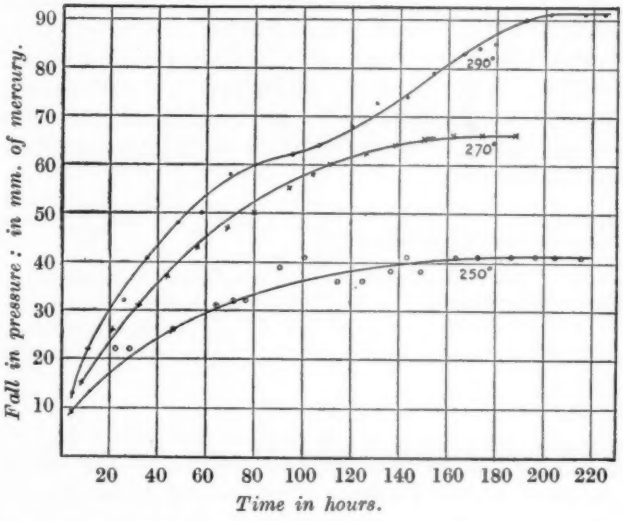
A thermometer, reading to 300°, was placed in the bath as shown. The whole of this apparatus was placed in a draught chamber so that the external conditions might be as uniform as possible.

In the first experiment, the bulb, filled with carbon monoxide but containing no catalyst, was heated to a constant temperature of 250° every day for a month; the total duration of heating was 225 hours. During this time, the manometer reading, corrected for variations in atmospheric pressure, showed apparent variations in pressure of the order of 1—3 mm. and always negative. The

pressures observed at the last two days of the experiment were within 1 mm. of that recorded at the beginning.

As the whole of the apparatus (bulb, etc.) was in a closed chamber —the surrounding air thus being kept at a rather higher temperature than that of the room—the slight decreases as recorded from time to time appear to be due to contractions in the volume of gas caused by the slight fall in the temperature of the air in the chamber when the readings were taken. This view is supported by the irregularity of the variation. Hence it was concluded that no real decrease in pressure had occurred and that the glass did not act as a catalyst for the reaction at 250°.

FIG. 3.



Carbon was introduced into the bulb, which was afterwards filled with carbon monoxide, all usual precautions being taken (see p. 2151) and a run of 100 hours was made at a constant temperature of 250°. No change of pressure was observed. Another similar run at a constant temperature of 300° gave no evidence of change of pressure in 58 hours. This evidently confirms the previous observation that with carbon as catalyst no carbon dioxide could be detected at temperatures below 300°.

Experiments were next performed with ignited, dry alumina as the catalyst. All due precautions being taken, the bulb was charged with alumina and carbon monoxide. The volume of gas in the bulb was arranged so that the level of the mercury in the manometer was almost equal to the level in the mercury reservoir,

the temperature being 250°. The bulb was then kept at a constant temperature of 250° until no further contraction in the volume of the gas took place. After the experiment was ended, the gas in the bulb was exhausted and passed through baryta water. Precipitation took place, proving the presence of carbon dioxide in the bulb.

Similar experiments were carried out at temperatures of 270° and 290°, all necessary precautions being taken in each case.

The results obtained in the three experiments are recorded graphically in Fig. 3.

The present work thus affords evidence that whilst carbon monoxide in contact with clean glass does not appreciably dissociate at 300°, the presence of certain catalysts, notably magnesium oxide and alumina, enables the reaction $2CO \longrightarrow CO_2 + C$ to proceed at temperatures below 300° and, in the case of alumina, as low as 250°. The extent of decomposition of carbon monoxide when equilibrium is attained in presence of alumina increases progressively with rise of temperature in the manner shown by the following figures:

Temperature	250°	270°	290°
Carbon monoxide decomposed (%) ...	5·35	8·50	12·25

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[*Received, May 17th*, 1926.]

CCLXXXV.—*A Differential Method for the Measurement of the Vapour Pressure of Liquids.*

By VICTOR GEORGE JOLLY and HENRY VINCENT AIRD BRISCOE.

FOR the purpose of some projected experiments on the intensive drying of liquids, it seemed desirable to find a method of measuring precisely the vapour pressure of a liquid without the use of a mercury manometer, the mercury column of which might be expected to retain traces of water and so retard complete drying. It seemed that such a method could be developed were the liquid itself to be used as the manometric liquid (compare Smith and Menzies, *J. Amer. Chem. Soc.*, 1910, **32**, 1412). Some advantages of the method are (1) that the measurements are made in the absence of any foreign gas, Campbell's results (*Trans. Faraday Soc.*, 1915, **10**, 197) having shown that the vapour pressure of a liquid is, in certain cases, substantially altered by the presence of a gas; (2)

that the use of a relatively light liquid as the manometric substance materially increases the accuracy of the determination; and (3) that in dealing with intensively dried liquids the vapour-pressure measurements would be made in a vessel of simple form which could be sealed off from the main apparatus and examined at leisure. The method finally evolved was to seal up the liquid, free from gas, in a simple U-tube, and then to observe the difference of level between the liquid in the two limbs maintained at different constant temperatures, and to repeat the observations for successive steps in temperature difference. Unfortunately, it seems impossible to establish absolute values without one such value for reference, but given that one value, the differential curve serves as a valuable check on existing curves and can be used to advantage where the

FIG. 1.

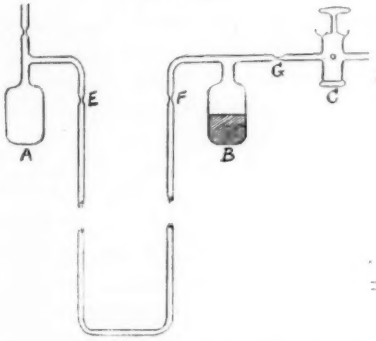
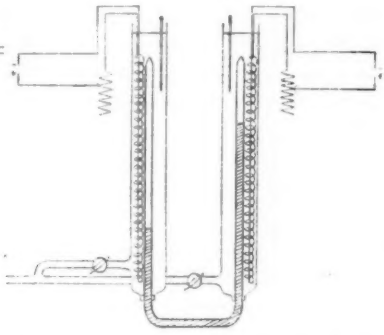


FIG. 2.



slope of the curve is of greater importance than the absolute position. The method was worked out and tested by experiments on benzene and water, and was then applied to a redetermination of the vapour-pressure curve for bromine. Such a redetermination seemed very desirable, as our knowledge of the vapour pressure of liquid bromine rests almost solely on the experiments of Ramsay and Young (J., 1886, **49**, 453).

The apparatus used consists essentially of a U-tube of about 6 mm. bore and with limbs about 60 cm. long and 10 cm. apart. The tube is filled with the liquid to be examined by means of a subsidiary apparatus which is sealed off prior to making the observations. The U-tube and filling apparatus are shown in Fig. 1. The purified liquid is placed in bulb A, frozen with a mixture of solid carbon dioxide and ether, and the apparatus exhausted through the mercury-sealed tap, C, by means of a mercury vapour pump. On being allowed to melt, the solid in A gives up the major part of the dissolved gases and by a sufficient number of

repetitions of this process the liquid can be rendered gas-free. A large number of experiments gave evidence that the process must be repeated at least three times, and that some liquids retain gas more persistently than others and may require to be frozen and melted in a vacuum six to eight times. When the liquid is almost gas-free, it is distilled slowly into B so as to drive before it any gas which may have been absorbed by the walls of the tube. Bulb A is then taken off by sealing the constriction E. The liquid, now in B, is again frozen, the apparatus exhausted as completely as possible, and the vacuum tap, C, removed by sealing at G. Finally, the liquid is distilled into the U-tube until the latter is a little more than half full, and the bulb B is disconnected by sealing the constriction F.

Fig. 2 shows the U-tube set up for measurements. The two limbs are enclosed in wide glass jackets filled with water, the temperature of which can be kept constant to within 0·05° by means of the internal heating coils. The water is stirred very efficiently by a steady stream of air. The temperature of the jackets is indicated by the two standardised thermometers readable to 0·01°.

The procedure is as follows. The temperature of the left-hand jacket is raised above that of the right-hand one until there is a considerable difference between the levels of the liquid in the two limbs of the U-tube. The temperature of each jacket is then kept constant for 30 minutes, by which time equilibrium is established, and the difference of levels read by means of a cathetometer reading to 0·01 mm. This is repeated after adjusting the temperature of the right-hand jacket to that which the left-hand one had in the previous case and again establishing a difference of levels by raising the temperature of the left-hand jacket. By this means one obtains a series of differential readings which can be reduced to mm. of mercury at 0°, account being taken of the change in density of the liquid with temperature.

Vapour Pressure of Benzene.

The data for benzene (Table I) obtained by this method illustrate clearly how the differential readings are transformed into mm. of mercury. The numbers (1) and (2) refer to the two limbs of the U-tube.

The benzene was purified by fractional distillation, the fraction used distilling within a range of 0·1°. The vapour pressure of benzene at 17·4° being accepted as 65·3 mm. Hg (Young, J., 1889, **55**, 486), the values at higher temperatures follow from the differential measurements. These are in Table II and are shown plotted against temperature in Fig. 3.

TABLE I.

Temp.		Height of column (cm.).		Density of benzene at temp. of jacket.		Height of equivalent column of water (cm.).		Differential *V. P.* in mm. Hg.
(1).	(2).	(1).	(2).	(1).	(2).	(1).	(2).	
23·6°	17·4°	10·52	46·02	0·874	0·880	9·20	40·53	23·20
29·2	23·6	8·33	48·50	0·868	0·874	7·23	42·38	26·04
33·5	29·2	10·03	47·34	0·863	0·868	8·66	41·10	24·03
37·2	33·5	10·84	46·96	0·859	0·863	9·31	40·53	23·13
40·8	37·2	8·77	49·10	0·855	0·859	7·50	42·18	25·69
43·7	40·8	10·80	47·67	0·852	0·855	9·20	40·76	23·37
46·5	43·7	9·53	48·92	0·849	0·852	8·09	41·68	24·88
48·8	46·5	11·43	47·47	0·846	0·849	9·68	40·30	22·69
51·3	48·8	8·93	49·82	0·844	0·846	7·54	42·18	25·66
53·2	51·3	12·73	46·72	0·842	0·844	10·72	39·43	21·27
54·8	53·2	13·63	46·12	0·840	0·842	11·45	38·84	20·29

TABLE II.

Temp.	23·6°	29·2°	33·5°	37·2°	40·8°	43·7°
V. P. (mm.) ...	88·5	114·5	138·6	161·7	187·4	210·8
Temp.	46·5°	48·8°	51·3°	53·2°	54·8°	
V. P. (mm.) ...	235·6	258·3	284·0	305·3	325·6	

It can be seen that even up to temperatures of 50° and above the new values fall well on Young's curve. It is noteworthy that any error in the method is cumulative, and if serious, would show more and more clearly as one approached the higher temperatures. Above 50°, it was found difficult to keep the temperature of the jackets within the set limits of constancy and therefore the determinations were not carried beyond that point.

Vapour Pressure of Water.

Similar experiments to the above were carried out with distilled water and yielded equally good results. These are in Table III and are plotted in Fig. 3, together with the accepted values (see Landolt-Börnstein, " Physikalisch-Chemische Tabellen," 1923).

TABLE III.

Temp.		Height of column (cm.).		Density of water at temp. of jacket.		Height of column corrected for density (cm.).		Differential *V. P.* in mm. Hg.
(1).	(2).	(1).	(2).	(1).	(2).	(1).	(2).	
33·8°	15·1°	10·40	45·55	0·994	0·999	10·34	45·51	25·89
43·7	33·8	10·20	47·05	0·991	0·994	10·11	46·76	26·98
49·4	43·7	13·70	44·30	0·988	0·991	13·54	43·90	22·36
51·9	43·7	5·20	51·50	0·987	0·991	5·13	51·10	33·83
26·9	15·1	20·10	38·65	0·996	0·999	20·02	38·61	13·69
39·1	26·9	11·10	46·35	0·992	0·996	11·01	46·16	25·87
46·8	39·1	11·60	45·95	0·989	0·992	11·48	45·57	25·09

In this case the assumed value for the vapour pressure is 12·91 mm. at 15·1°, taken from the accepted curve; it is evident that the method again holds good over the temperature range covered by the experiments, *viz.*, 15—50°. Table IV gives the actual vapour pressures derived from the differential results.

TABLE IV.

Temp.	26·9°	33·8°	39·1°	43·7°	46·8°	49·4°	51·9°
V. P. (mm.)	26·6	38·8	52·5	65·8	77·6	88·1	99·6

FIG. 3.

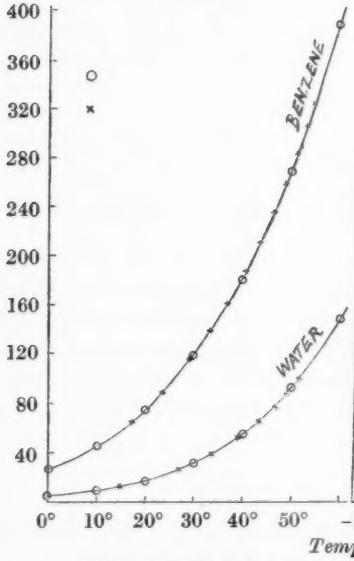
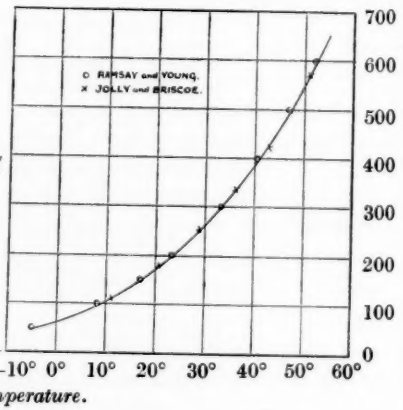


FIG. 4.



Temperature.

⊙ { *Accepted values for water.* / *Young's values for benzene.*
× *Differential values.*

Ordinates represent V. P. in mm. Hg.

Redetermination of the Vapour Pressure of Bromine.

At first it was supposed that if one could obtain a series of differential vapour pressures, construct a curve on some assumed value, and extrapolate to some low temperature at which the vapour pressure is sensibly zero (*i.e.*, within the experimental error), then it would be possible to determine the error of the assumed value. The assumed curve, being constructed from differential measurements, would have the correct slope but probably the wrong absolute position. Hence, by shifting it bodily by an amount equal to the

difference between the extrapolated value at the very low temperature and zero pressure, the true curve for bromine could be obtained.

An attempt was made to do this, but instead of plotting pressure against temperature, the latter was plotted against $T \log p$, a straight line resulting. Although this could be extrapolated easily to lower temperatures, it deviated in the region of $-60°$ and beyond, turning towards $-\infty$ and thus leading to erroneous conclusions. It is about the temperature of $-60°$ that the vapour pressure of bromine can be assumed to be zero.

It became necessary, therefore, to get some independent value for the pressure at any one temperature in order to fix the absolute position of the vapour-pressure curve; the value accepted was that of Ramsay and Young at 20·7°, namely, 178·7 mm. of mercury.

The bromine used for the differential measurements was purified and dried by distillation successively from potassium bromide and concentrated sulphuric acid, the head and tail fractions being rejected in each case. The differential measurements are shown in Table V.

TABLE V.

Temp.		Height of column (cm.).		Density of bromine at temp. of jacket.		Height of equivalent column of water (cm.).		Differential *V. P.* in mm. Hg.
(1).	(2).	(1).	(2).	(1).	(2).	(1).	(2).	
20·7°	11·1°	16·45	45·40	3·117	3·152	51·28	143·10	67·57
28·9	20·7	14·75	47·67	3·088	3·117	45·55	148·60	75·80
36·1	28·9	13·62	49·85	3·064	3·088	41·73	153·90	82·50
42·8	36·1	12·76	51·13	3·041	3·064	38·80	156·70	86·78
47·2	42·8	14·44	49·55	3·026	3·041	43·70	150·70	78·75
51·0	47·2	17·13	47·65	3·012	3·026	51·60	144·20	68·16

On combining Ramsay and Young's value at 20·7° with the differential values the following absolute values were obtained :

Temp.	11·1°	20·7°	28·9°	36·1°	42·8°	47·2°	51·0°
V. P. (mm.)	111·1	178·7	254·5	337·0	423·8	502·5	570·7

Fig. 4 shows these values plotted together with those of Ramsay and Young. It is evident that the form of Ramsay and Young's curve is closely confirmed by the differential measurements.

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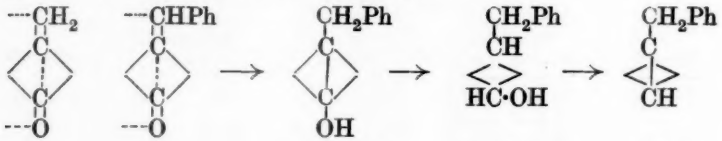
NEWCASTLE-UPON-TYNE. [*Received, May 29th,* 1926.]

CCLXXXVI. — *The Reactivity of* meso-*Substituted Anthracenes. Part III.*

By JAMES WILFRED COOK.

IT has been shown that, when an unsaturated or negative substituent is attached to one of its *meso*-carbon atoms, the capacity of an anthracene derivative to enter into reactions of 9 : 10-addition is greatly lessened and in a former communication (this vol., p. 1282) it was foreshadowed that this limitation would be removed when the *meso*-substituent is saturated. This hypothesis has been fairly well substantiated by a comparison of 9-benzoylanthracene with 9-benzylanthracene, the reactions of which are now described.

9-Benzylanthracene (V) was obtained in an impure state by Bach (*Ber.*, 1890, **23**, 1567) by the reduction of benzylhydroxyanthrone or of benzylideneanthrone (II) with hydriodic acid and red phosphorus. Barnett and Matthews (*Ber.*, 1926, **59**, 767) have shown that reduction of methyleneanthrone (I) leads to union of the methylene carbon atoms of two molecules, a reaction which suggests that the methylene carbon atom and the carbonyl oxygen atom are endowed with free residual affinity:

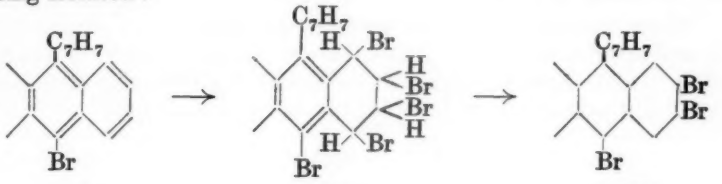


(I.) (II.) (III.) (IV.) (V.)

In the case of benzylideneanthrone (II) steric factors prevent union of two molecules, but there seems little doubt that the distribution of free residual affinity is similar, since reduction with zinc and acetic anhydride leads to the production of the acetate of benzylanthranol (III). Reduction of benzylideneanthrone proceeds a stage further when zinc dust and ammonia are used, so that the benzylanthranol first formed is converted into benzyldihydroanthranol (IV), which is considerably more stable than 9 : 10-dihydroanthranol but loses water across the ring under the influence of acetic acid and passes into benzylanthracene (V). Since benzylideneanthrone is readily obtained by condensing anthrone with benzaldehyde, benzylanthracene is conveniently obtained by the above series of reactions. If this mechanism of the reactions involved be accepted, the position of the hydroxyl group in benzyldihydroanthranol (IV) follows, in conformity with the orientation given by Bach (*Ber.*, 1890, **23**, 2527), although not in agreement with Tschilikin (*ibid.*, 1914, **47**, 1055), and the fact that the sub-

stance is more stable than dihydroanthranol can scarcely be attributed to steric influences. The reduction of methyleneanthrone and its derivatives is thus analogous to that of anthraquinone derivatives and in the former case the course taken by the reaction cannot be explained on the basis of a peroxide structure but must be due to conjugation (compare Barnett and Matthews, *loc. cit.*). The production of dianthranol and not dianthrone by the reduction of dianthraquinone (Matthews, this vol., p. 236) lends further support to this view of the mechanism.

9-Benzylanthracene resembles anthraphenone in yielding no stable additive compound with bromine, the product of the reaction with 1 mol. of bromine being 10-bromo-9-benzylanthracene (VI). Bromination probably proceeds through the intermediate formation of an additive compound, however, since if the reaction is carried out in the presence of excess of bromine the benzyl group is lost before re-establishment of the " bridge " occurs and 9 : 10-dibromoanthracene results. That this is not due to the action of bromine on bromobenzylanthracene is shown by the fact that the latter compound gives a tetrabromide (VII) when treated with bromine under the same experimental conditions, no dibromoanthracene being isolated :



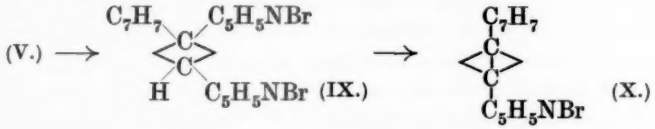
(VI.) (VII.) (VIII.)

The facile addition of bromine to the benzene ring suggests that introduction of the *meso*-bromine atom favours the ortho-quinonoid structure of the anthracene ring, and similar addition of bromine has been observed with other *meso*-disubstituted anthracenes in which at least one substituent is negative (Barnett and Matthews, *Ber.*, 1926, **59**, 1429). With other disubstituted anthracenes, no such addition occurs, 9 : 10-dibenzylanthracene, for example, being brominated in the benzyl groups (Lippmann and Pollak, *Monatsh.*, 1902, **23**, 672; Lippmann and Fritsch, *Annalen*, 1907, **351**, 52).

Bromobenzylanthracene tetrabromide (VII) is converted by treatment with an alcoholic solution of potassium hydroxide into 2 : 3 : 10-tribromo-9-benzylanthracene (VIII), the orientation of which is shown by its oxidation to 2 : 3-dibromoanthraquinone.

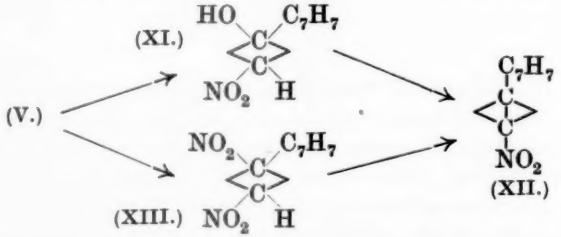
Further evidence that bromination of benzylanthracene is preceded by addition is afforded by the observation that a dipyridinium dibromide (IX) is formed when benzylanthracene is treated with

pyridine perbromide in pyridine solution. In fact, the action of this reagent illustrates in a very striking manner the transition from 9 : 10-additive power to direct replacement at 10 as the substituent in the 9-position of the anthracene molecule becomes increasingly negative in character, for 9-benzoylanthracene (anthraphenone) is unattacked under the same conditions, whilst 9-phenylanthracene is readily converted into 10-bromo-9-phenylanthracene. Benzyldihydroanthraquinyldipyridinium dibromide (IX) loses pyridine hydrobromide under the influence of acid or alkaline reagents and passes into benzylanthranylpyridinium bromide (X) (compare Barnett and Cook, J., 1921, **119**, 901) :



The action of chlorine on benzylanthracene leads to the production of 10-chloro-9-benzylanthracene, and the same product is obtained when chlorination is effected by means of sulphuryl chloride, although in the latter case a considerable amount of 9 : 10-dichloroanthracene is also formed.

When treated with nitric acid in the presence of acetic acid, benzylanthracene yields a moderately stable additive compound (XI), which, however, loses water under the influence of mineral acids and passes into 10-nitro-9-benzylanthracene (XII) :

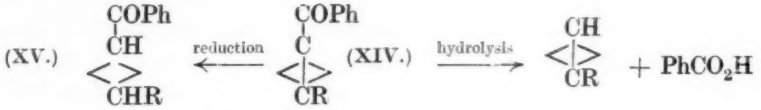


Anthracene itself under similar conditions gives only the acetate of the nitrodihydroanthranol (Meisenheimer and Connerade, *Annalen*, 1904, **330**, 133; Barnett, Cook, and Matthews, J., 1923, **123**, 1994) and the diminished reactivity of the free hydroxy-compound obtained from benzylanthracene is probably due to steric hindrance and has been observed with the corresponding additive compound of 9-ethylanthracene (Meisenheimer and Connerade, *loc. cit.*). The extreme sensitivity of benzylnitrodihydroanthranol (XI) to mineral acids in contrast to its stability towards other reagents is significant and suggests that the non-isolation of

additive compounds in certain other cases should not be taken as proof of general instability.

Addition of nitrogen dioxide to benzylanthracene is readily effected and although the resulting compound (XIII) could not be obtained pure its identity was established by its conversion into nitrobenzylanthracene (XII) under the influence of cold pyridine.

In former parts of this series (this vol., pp. 1282, 1677), it was shown that anthraphenone and 10-benzoylanthraphenone are readily reduced to the corresponding dihydroanthracene derivatives and that benzoylanthraphenone, unlike anthraphenone, does not easily lose a benzoyl group by hydrolysis. The suggestion was made that the greater stability of benzoylanthraphenone is due to the suppression of *meso*-additive power by the attachment of the unsaturated benzoyl group to the carbon atom in position 10, and in order to test this hypothesis 10-benzylanthraphenone and 10-phenylanthraphenone have now been examined.



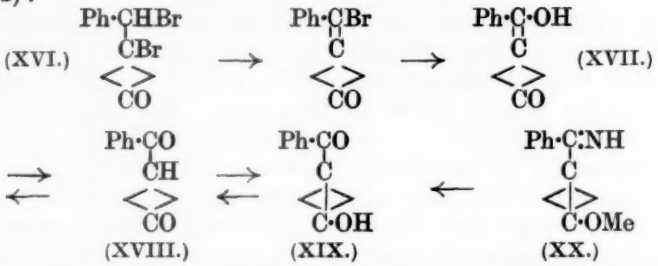
(R = C_7H_7, C_6H_5·CO, C_6H_5, or H.)

Both compounds are reduced to the dihydroanthracene derivatives only with difficulty and the retarding influence of the substituent in position 10 is readily explicable on the theory of steric hindrance and is further evidence of primary addition to the carbonyl oxygen atoms in the case of benzoylanthraphenone. As was foreseen, the more saturated nature of the benzyl group resulted in benzylanthraphenone being hydrolysed under conditions in which benzoylanthraphenone was not affected, but with phenylanthraphenone the result was unexpected, this compound undergoing hydrolysis also. At present, no satisfactory explanation can be given of this anomaly.

Benzyldihydroanthracene is conveniently obtained by reducing benzylanthracene with sodium and amyl alcohol and is more stable than dihydroanthracene, being recovered unchanged after treatment with bromine or with nitric acid under conditions which lead to reaction in the case of dihydroanthracene. The benzyl group has a greater influence than an ethyl group in stabilising the dihydroanthracene derivative, since Meisenheimer and Connerade (*loc. cit.*) have shown that ethyldihydroanthracene is readily attacked by nitric acid in acetic acid even at 0°.

It was shown in Part II of this series that 9 : 10-dihydroanthraphenone is a tautomeric compound and it seemed of interest to

study the cyclol-keto-enol tautomerism which benzoylanthrone (XVIII) might feasibly exhibit. This substance was obtained by Krollpfeiffer (*Ber.*, 1923, **56**, 2360) by hydrolysis of 10-methoxy-9-anthranylphenylketimide (XX). Krollpfeiffer gave no experimental details and it seemed probable that benzoylanthrone would be obtained more conveniently from benzylideneanthrone dibromide (XVI):



Up to the present, a satisfactory method for bringing about the first stage of the reaction has not been devised, treatment of the dibromide with pyridine, diethylamine, aqueous acetone, alcohol or dry silver oxide leading to loss of bromine and the formation of benzylideneanthrone as the main product of the reaction. With moist silver oxide, however, the reaction appeared to take the desired course and a product was obtained which gave analytical figures agreeing with those required for hydroxybenzylideneanthrone (XVII) or benzoylanthrone (XVIII), yielded a monoacetyl derivative when treated with acetic anhydride in the presence of pyridine, and dissolved in aqueous sodium hydroxide to give a deep red solution, presumably of the sodium salt of benzoylanthranol (XIX). Since these experiments were carried out, it has been found that the tautomerism of benzoylanthrone has been investigated by Thorn (Dissertation,* Marburg, May 1924) and the study of this subject has therefore been postponed. It seemed desirable, however, to place on record the above results, since the properties of the compound obtained by the action of silver hydroxide on benzylideneanthrone dibromide indicate that it is certainly not the benzoylanthrone obtained by Krollpfeiffer (*loc. cit.*) and Thorn.

Experimental.

Benzylideneanthrone (II) was obtained by Levi (*Ber.*, 1885, **18**, 2152), Bach (*ibid.*, 1890, **23**, 1567), Padova (*Compt. rend.*, 1905, **141**, 857; *Ann. Chim.*, 1910, **19**, 353), and Tschilikin (*Ber.*, 1914, **47**,

* I am indebted to Dr. E. de Barry Barnett for placing at my disposal a copy of this dissertation, which was kindly lent to him by Prof. F. Krollpfeiffer.

1055) by dehydration of benzylhydroxyanthrone, and by Padova (*loc. cit.*) in 38% yield by condensing benzaldehyde with anthrone. The latter method is more convenient and by using the following simplification of Padova's method a 65% yield of pure benzylideneanthrone was obtained.

Anthrone (200 g.), benzaldehyde (125 c.c.), pyridine (500 c.c.), and piperidine (5 c.c.) were boiled together for 4 hours; 375 c.c. of the solvent were removed by distillation and alcohol (300 c.c.) was added to the residue. After cooling, the resulting solid was collected and recrystallised from alcohol; it then melted at 127° in agreement with Levi, Bach, and Padova, although Tschilikin gives the m. p. as 117°.

Reduction of Benzylideneanthrone.—(*a*) Benzylideneanthrone (10 g.) was heated at 150—155° for 5 hours with zinc dust (20 g.) and acetic anhydride (100 c.c.). The excess of zinc dust was filtered off and the crystals which separated from the filtrate on cooling were collected and recrystallised from glacial acetic acid, then from alcohol and finally from benzene and light petroleum (Found: C, 84·6; H, 5·7. $C_{23}H_{18}O_2$ requires C, 84·7; H, 5·5%). 9-*Benzylanthranyl* 10-*acetate* forms colourless, glistening needles, m. p. 210—211°. It is readily soluble in acetic acid and in benzene and its solutions have an intense violet fluorescence. It is hydrolysed by alcoholic potassium hydroxide, giving the deep orange colour characteristic of an anthranol.

(*b*) An intimate mixture of benzylideneanthrone (50 g.) and zinc dust (150 g.) was heated on the water-bath with 500 c.c. of concentrated ammonia diluted with 250 c.c. of water. The zinc dust was activated by the addition of a little copper sulphate solution. At first, the solution assumed a deep orange colour, but became colourless after 1½ hours. Heating was continued for a further ½ hour, and the solid collected, dried between filter-paper, and extracted with 500 c.c. of boiling benzene. After filtering off the zinc dust, the benzene solution was concentrated and light petroleum added. On cooling, 45 g. of pure 10-hydroxy-9-benzyl-9 : 10-dihydroanthracene (IV) separated. It formed colourless needles, m. p. 122—125° (compare Bach, *Ber.*, 1890, **23**, 2527; Tschilikin, *loc. cit.*). Benzyldihydroanthranol is readily soluble in alcohol and its solutions are devoid of fluorescence. It is completely converted into benzylanthracene by boiling with acetic acid, but differs from 9 : 10-dihydroanthranol in being only partly dehydrated by heating with aqueous sodium hydroxide or hydrochloric acid.

When treated with acetic anhydride in pyridine at the ordinary temperature, benzyldihydroanthranol gave a product which melted at 80° after recrystallisation from alcohol, but further attempts at

purification led to conversion into benzylanthracene. The substance was undoubtedly an acetate of the dihydroanthranol, since it gave a strong smell of ethyl acetate when heated with sulphuric acid and alcohol. Dihydroanthranol itself is merely converted into anthracene by this treatment. Benzyldihydroanthranol gave only benzylanthracene and carbanilide when treated with phenylcarbimide in boiling benzene solution.

(*c*) When benzylideneanthrone was reduced with zinc dust and acetic acid, with zinc and hydrochloric acid, or with tin and hydrochloric acid in glacial acetic acid solution, only resinous products were obtained.

9-Benzylanthracene.

A solution of benzyldihydroanthranol (90 g.) in acetic acid (600 c.c.) was boiled for $\frac{3}{4}$ hour. On cooling, pure benzylanthracene (65 g.) separated. For analysis, a sample was recrystallised from alcohol and formed colourless needles, m. p. 133° (Bach, *loc. cit.*, gives the m. p. as 119°). Benzylanthracene is but sparingly soluble in alcohol and its solutions have a violet fluorescence. As stated by Bach, it dissolves in sulphuric acid, giving a dark green solution with a red fluorescence (Found : C, 93·8; H, 6·1. Calc. : C, 94·0; H, 6·0%).

Action of Bromine.—(*a*) A solution of benzylanthracene in carbon disulphide readily absorbed bromine (1 mol.), hydrogen bromide being liberated. After evaporation of the solvent the residual *10-bromo-9-benzylanthracene* (VI) was recrystallised from acetic acid and obtained as lemon-yellow needles, m. p. 144° (Found : Br, 22·8. $C_{21}H_{15}Br$ requires Br, 23·0%). The compound obtained in this way by Bach (*loc. cit.*) decomposed at 113—114°, which suggests that anthracene was present in his benzylanthracene and that his bromo-compound was contaminated with the unstable anthracene dibromide.

(*b*) When 2 or 3 mols. of bromine were used in the above preparation, bromine was still present after the solution had been kept at the ordinary temperature for several hours. The solvent was evaporated and the resinous product triturated with cold alcohol. By the addition of alcohol to a solution of the residue in pyridine, lemon-yellow needles were obtained which, after recrystallisation from benzene, melted at 220° alone or when mixed with 9 : 10-dibromoanthracene (Found : Br, 47·5. Calc. : Br, 47·6%).

(*c*) Bromine (2 c.c.; 2 mols.) was added to a solution of 10-bromo-9-benzylanthracene (6·5 g.) in carbon disulphide (50 c.c.), and the solution kept over-night at the ordinary temperature. The solution was washed with dilute aqueous sodium hydroxide and with water, and the solvent allowed to evaporate. The resinous product was

triturated with ether; the 2·5 g. of a colourless solid remaining were recrystallised from chloroform and ether (Found: Br, 60·1. $C_{21}H_{15}Br_5$ requires Br, 60·0%).

10-*Bromo*-9-*benzylanthracene tetrabromide* (VII) forms a colourless, crystalline powder, m. p. 192° (decomp.).

On one occasion, the ethereal solution, after the above tetrabromide had been filtered off, slowly deposited crystals; these, on recrystallisation from benzene and light petroleum, formed colourless needles of constant m. p. 127° (decomp.). The substance was evidently one of the stereoisomeric tetrabromides, but could not be investigated, as it was never isolated again (Found: Br, 60·0%).

The tetrabromide melting at 192° (1 g.) was heated for 2 hours on the water-bath with alcohol (25 c.c.) to which had been added a concentrated aqueous solution of potassium hydroxide (2 g.). The resulting yellow solid was recrystallised from pyridine and alcohol and then from methyl ethyl ketone (Found: Br, 47·4. $C_{21}H_{13}Br_3$ requires Br, 47·5%).

2 : 3 : 10-*Tribromo*-9-*benzylanthracene* (VIII) forms silky, yellow needles, m. p. 206—207°. Its solutions have a violet fluorescence. By oxidation with chromic acid in acetic acid, this tribromo-compound yielded a product which contained bromine and melted at 279—280° alone or when mixed with authentic 2 : 3-dibromoanthraquinone (Barnett and Cook, J., 1925, **127**, 1489).

Action of Pyridine Perbromide.—To a suspension of benzylanthracene (2·7 g.) in pyridine (6 c.c.) was added a solution of bromine (0·5 c.c.; 1 mol.) in pyridine (4 c.c.). After 2 hours, the solid in suspension was collected and washed with pyridine and with ether. It was recrystallised from 10 c.c. of warm (not boiling) water, dried in a vacuum desiccator, and finally recrystallised from anhydrous alcohol with the addition of anhydrous ether (Found: Br, 25·3. $C_{31}H_{26}N_2Br_2,C_2H_6O$ requires Br, 25·3%). 9-*Benzyl*-9 : 10-*dihydroanthraquinyl*-9 : 10-*dipyridinium dibromide* (IX) forms a snow-white, crystalline powder which melts to a yellow liquid at 138—140°. The presence of alcohol of crystallisation was shown by the ethyl acetate reaction.

This dibromide was decomposed by boiling water with the production of a resinous substance which dissolved in aqueous sodium hydroxide with the orange-red colour of an anthranol (compare Barnett and Cook, J., 1921, **119**, 901). By the action of boiling aniline or of warm dilute mineral acids the dibromide lost pyridine hydrobromide and passed into 9-*benzylanthranyl*-10-*pyridinium bromide* (X). This substance was precipitated by the addition of dilute ammonium hydroxide solution to an aqueous solution of the dibromide and was recrystallised from water (from which it separated

as a heavily hydrated curd) and afterwards from alcohol (Found: Br, 18·6. $C_{26}H_{20}NBr$ requires Br, 18·8%). This bromide forms fluffy, yellow needles, m. p. 226°. It is sparingly soluble in water and is stable towards boiling water, but gives coloured products with sodium hydroxide.

Anthraphenone was treated with pyridine perbromide under the conditions described above and was recovered unchanged. If 2 mols. of bromine were employed and the solution was kept at the ordinary temperature for several days, 10-bromoanthraphenone (this vol., p. 1282) was obtained.

9-Phenylanthracene, treated for 2 hours with a solution of bromine (1 mol.) in pyridine under the conditions described for benzylanthracene, was converted into *10-bromo-9-phenylanthracene*, which, after recrystallisation from acetic acid and from methyl ethyl ketone and alcohol, formed glistening, yellow leaflets, m. p. 154—155° (Found: Br, 24·0. $C_{20}H_{13}Br$ requires Br, 24·0%). The same product was obtained when a solution of phenylanthracene in carbon disulphide or chloroform was treated with bromine at the ordinary temperature, and the position of the bromine atom was shown by the production of phenylhydroxyanthrone (compare Barnett and Cook, J., 1923, **123**, 2638) by oxidation with chromic acid in acetic acid solution.

Action of Chlorine.—9-Benzylanthracene, suspended in carbon tetrachloride, was treated with a solution of chlorine (1 mol.) in carbon tetrachloride. Reaction took place rapidly with the liberation of hydrogen chloride and the formation of *10-chloro-9-benzylanthracene*, which crystallised from amyl alcohol in yellow needles, m. p. 127—128° (Found: Cl, 11·7. $C_{21}H_{15}Cl$ requires Cl, 11·7%).

The same product was formed, mixed with 9 : 10-dichloroanthracene, when a solution of benzylanthracene (2·7 g.) in chloroform (10 c.c.) was heated on the water-bath for an hour with sulphuryl chloride (2 c.c.). The dichloroanthracene separated on cooling and was identified by direct comparison with an authentic sample. The chlorobenzylanthracene remained in solution and was only obtained pure after repeated recrystallisation.

Action of Nitric Acid.—Nitric acid (*d* 1·4; 0·4 c.c.) was added to a suspension of benzylanthracene (1·35 g.) in acetic acid (5 c.c.). The benzylanthracene rapidly dissolved and after keeping at the ordinary temperature for 2 hours the colourless solid which had separated was washed with a little acetic acid and crystallised from benzene and light petroleum (Found: C, 76·0; H, 5·3. $C_{21}H_{17}O_3N$ requires C, 76·1; H, 5·1%). *9-Hydroxy-10-nitro-9-benzyl-9 : 10-dihydroanthracene* (XI) forms colourless needles, m. p. 160° (with evolution of gas). It was not attacked by brief boiling with sodium

hydroxide in aqueous or alcoholic solution and was but slightly decomposed by pyridine at 100°. With mineral acids in acetic acid solution, however, the substance lost water and passed into 10-nitro-9-benzylanthracene (XII) (see later). When hydriodic acid was used, this dehydration occurred rapidly at the ordinary temperature and was accompanied by very little reduction.

Action of Nitrogen Dioxide.—The gas, prepared by heating lead nitrate, was led into a suspension of benzylanthracene (5 g.) in chloroform (10 c.c.) cooled in a freezing mixture. After 2·4 g. of nitrogen dioxide had been taken up, the clear solution was kept in the freezing mixture for an hour and light petroleum was then added. An oil separated which refused to solidify. It was therefore dissolved in a mixture of pyridine (5 c.c.) and alcohol (10 c.c.) and kept over-night at the ordinary temperature. The orange crystals which separated were recrystallised from acetic acid, then from pyridine and alcohol, and finally from amyl alcohol (Found : N, 4·6. $C_{21}H_{15}O_2N$ requires N, 4·5%). 10-*Nitro*-9-*benzylanthracene* (XII) forms slender, golden-yellow needles, m. p. 178—180°.

Reduction of Benzylanthracene.—Sodium (1 g.) was added to a boiling solution of benzylanthracene (2·5 g.) in amyl alcohol (10 c.c.). After the sodium had dissolved, the hot solution was poured into water, and the solid collected and recrystallised from alcohol. It melted at 119—120°, alone or mixed with the 9-benzyl-9 : 10-dihydroanthracene obtained by the reduction of dihydroanthraphenone (this vol., p. 1677).

Benzyldihydroanthracene was recovered unchanged after its solution in carbon disulphide containing an excess of bromine had been kept for 2 hours at the ordinary temperature. 9 : 10-Dihydroanthracene yields 9 : 10-dibromoanthracene under these conditions.

A suspension of benzyldihydroanthracene in acetic acid was treated with nitric acid (*d* 1·4; 2 mols.) and kept over-night at the ordinary temperature. No reaction took place.

Derivatives of Anthraphenone.

Benzylanthraphenone (XIV).—A solution of benzylanthracene (15 g.) in carbon disulphide (100 c.c.) was treated with anhydrous aluminium chloride (15 g.) followed by benzoic anhydride (15 g.). After heating on the water-bath for 6 hours, the aluminium compound was decomposed with cold dilute hydrochloric acid, and the carbon disulphide removed with steam. The residue was extracted with sodium hydroxide solution and recrystallised from benzene and afterwards from benzene and light petroleum (Found : C, 90·1; H, 5·5. $C_{28}H_{20}O$ requires C, 90·3; H, 5·4%).

10-*Benzylanthraphenone* forms a cream-coloured, crystalline pow-

der, m. p. 237°. In common with other anthraphenone derivatives, its solutions are not fluorescent. It dissolved in sulphuric acid with a cornflower-blue colour which soon changed to dark green, and at the same time the characteristic dark red fluorescence of benzylanthracene was developed. That fission had occurred was shown by the fact that benzoic acid was isolated from the diluted solution. Benzylanthraphenone was decomposed with the production of tarry matter by ½ hour's boiling with sulphuric acid in acetic acid, and benzylanthracene gave similar products under these conditions.

Benzylanthraphenone was not reduced by boiling for 6 hours with zinc dust and acetic acid or by heating with zinc dust and ammonia, although some slight reduction was effected with zinc dust and hydrochloric acid in acetic acid. Partial reduction was also brought about by boiling a solution of the ketone (2·5 g.) in acetic acid (25 c.c.) with 50% hydriodic acid (2·5 c.c.) and red phosphorus (0·65 g.) for 5 hours. After cooling, the excess of phosphorus and the unchanged material were filtered off and the filtrate was diluted with water. The resinous product was obtained pure after two recrystallisations from alcohol and then gave no colour with sulphuric acid (Found : C, 89·5; H, 5·9. $C_{28}H_{22}O$ requires C, 89·8; H, 5·9%). 10-*Benzyl*-9 : 10-*dihydroanthraphenone* (XV) forms yellow needles, m. p. 171—172°.

Phenylanthraphenone (XIV).—The phenylanthracene used in this preparation was obtained by the action of magnesium phenyl bromide on anthrone, the excess of anthrone being removed by extraction with boiling aqueous sodium hydroxide. The method is simpler than that previously described (Barnett and Cook, J., 1923, **123**, 2638), but the yields are poor.

Phenylanthracene (12·5 g.) suspended in carbon disulphide (80 c.c.) was treated with aluminium chloride (15 g.) and benzoic anhydride (16 g.) in the manner described for the benzyl compound. The crude product, after extraction with alkali, was recrystallised from acetic acid and yielded 14 g. of pure phenylanthraphenone. For analysis, a sample was recrystallised twice from benzene and light petroleum and then formed a cream-coloured, crystalline powder, m. p. 218—219° (Found : C, 90·7; H, 5·2. $C_{27}H_{18}O$ requires C, 90·5; H, 5·0%).

10-*Phenylanthraphenone* gives a transient cornflower-blue colour when dissolved in sulphuric acid and undergoes fission when boiled for ¾ hour with sulphuric acid (1 part) in acetic acid (10 parts), pure phenylanthracene separating from the solution on cooling.

A suspension of phenylanthraphenone (2 g.) in acetic acid (25 c.c.) was boiled for 4 hours with zinc dust (4 g.). After cooling, the unchanged material and the excess of zinc dust were removed, water

was added to the filtrate, and the resulting precipitate recrystallised from alcohol and then from benzene and light petroleum (Found: C, 89·7; H, 5·7. $C_{27}H_{20}O$ requires C, 90·0; H, 5·6%).

10-*Phenyl*-9 : 10-*dihydroanthraphenone* (XV) forms colourless, silky needles, m. p. 165°, and gives no colour with sulphuric acid.

Very little reduction took place when phenylanthraphenone was boiled with hydriodic acid and phosphorus in acetic acid.

Benzylideneanthrone Dibromide (XVI).

Attempts to prepare bromobenzylideneanthrone by boiling this dibromide with alcohol or with alcohol and water were fruitless, the only products isolated being benzylideneanthrone and anthraquinone (compare Bach, *Ber.*, 1890, **23**, 1567). Loss of bromine also took place when a solution of the dibromide in benzene was boiled with diethylamine or with dry silver oxide, and a similar result was obtained with aqueous acetone in the presence of calcium carbonate and with pyridine in the presence of acetic anhydride (coloured resinous products were obtained with pyridine alone).

Action of Silver Oxide.—Water (20 c.c.) was added to a solution of benzylideneanthrone dibromide (10 g.) in acetone (100 c.c.), followed by the silver oxide prepared from 10 g. of silver nitrate. After keeping at the ordinary temperature for 3 hours, the whole was heated to boiling, filtered, and the filtrate diluted with water. The resulting solid (2·6 g.) was twice recrystallised from alcohol and obtained as colourless needles, m. p. 133—134° (Found: C, 84·5; H, 4·75. $C_{21}H_{14}O_2$ requires C, 84·6; H, 4·7%). This *compound* gave a magenta solution in sulphuric acid and a blood-red colour with aqueous or alcoholic sodium hydroxide. It was not decomposed by alcoholic sodium hydroxide under conditions which sufficed for the hydrolysis of 9 : 10-dihydroanthraphenone, or by sulphuric acid in acetic acid under conditions which led to hydrolysis of anthraphenone (compare Cook, *loc. cit.*).

By heating the above compound (1 g.) on the water-bath for an hour with acetic anhydride (1 c.c.) and pyridine (2 c.c.), an *acetate* was obtained which, after recrystallisation from alcohol and then from benzene and light petroleum, formed colourless nodules, m. p. 140—141° (Found: C, 81·0; H, 4·8. $C_{23}H_{16}O_3$ requires C, 81·2; H, 4·7%).

The author desires to express his thanks to Dr. E. de Barry Barnett for gifts of materials.

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LONDON, E.C. 3. [*Received, May 13th,* 1926.]

CCLXXXVII.—*The Chemistry of the Glutaconic Acids. Part XX. Tetrahydroisophthalic Acid.*

By Ernest Harold Farmer and Henry Lorimer Richardson.

In connexion with an examination of the structural mobility exhibited by cyclic systems containing the acylcrotonic grouping $\cdot CH_2 \cdot CO \cdot CH_2 \cdot CH{:}CH \cdot CO_2H$, it has become necessary, for purposes of comparison, to study the tautomeric capacity of the closely allied Δ^2-tetrahydro*iso*phthalic acid (I). This substance, in form an $\alpha\gamma$-disubstituted glutaconic acid, was obtained along with its Δ^3- and Δ^4-isomerides by Perkin and Pickles (J., 1905, **87**, 293) in an investigation of the reduction products of *iso*phthalic acid. The interconvertibility of the four isomeric tetrahydro-acids was explored by these authors and formulæ were assigned on the basis of the observations; the presence or absence of glutaconic tautomerism in the Δ^2-acid, however, was not determined. Owing to the number of substituents, this acid should not show the highest degree of glutaconic mobility, but would reasonably be expected to resemble in behaviour $\alpha\gamma$-dimethylglutaconic acid.

The ester of Perkin and Pickles's Δ^2-acid cannot be methylated under any conditions. Further, the methods applicable to the glutaconic acids have repeatedly failed to yield a hydroxy-anhydride, although the ordinary anhydride, as shown by the above authors, is readily obtainable. The acid, therefore, does not display two of the most important characteristics of glutaconic compounds. Whilst, however, with glutaconic acid, fixity of structure should result in geometrical isomerism, a semi-cyclic substance of formula (I) should exist in but one form whether the constitution be fixed, or mobile

(I.) $CH_2\!<\!\begin{matrix}CH_2\cdot CH(CO_2H)\\ CH_2\!-\!C(CO_2H)\end{matrix}\!>\!CH$ $\quad$ $CH_2\!<\!\begin{matrix}CH_2\!-\!-C(CO_2H)\\ CH_2\cdot CH(CO_2H)\end{matrix}\!>\!CH$ (II.)

(III.) $CH_2\!<\!\begin{matrix}CHR\cdot CH(CO_2H)\\ CH_2\!-\!C(CO_2H)\end{matrix}\!>\!CH$ $\quad$ $CH_2\!<\!\begin{matrix}CH_2\cdot CH(CO_2X)\\ CH_2\!-\!C(CO_2X')\end{matrix}\!>\!CH$ (IV.)

$$CH_2\!<\!\begin{matrix}CH_2\cdot CH(CO_2H)\\ CH_2\!=\!C(CO_2H)\end{matrix}\!>\!CH_2 \quad \text{(V.)}$$

within the limits of the glutaconic three-carbon system. Distinction between the forms (I) and (II) is only to be perceived when the molecule is rendered unsymmetrical as in (III) or (IV). In testing the mobility of Perkin and Pickles's Δ^2-acid, the device represented in (IV) has been adopted, the half-ester of the acid being employed.

When the anhydride of the tetrahydro-acid is heated with ethyl alcohol, not one, but two crystalline forms of the ethyl hydrogen ester are obtained, just as with *as*-dimethylsuccinic anhydride two

forms of the corresponding ethyl hydrogen succinate are produced. Also, as with *as*-dimethylsuccinic anhydride, treatment with methyl alcohol yields one crystalline methyl hydrogen ester and only a trace of oily material which might represent a second form. When, however, bromine is added to this crystalline form and the product is treated with diethylamine, a somewhat impure monobromo-compound is obtained which yields on reduction a mixture of the original solid acid ester and a new substance; the latter appears to be the isomeric methyl hydrogen ester. There is, therefore, strong evidence of fixity of structure in the acid to which the formula (I) has been assigned, the forms (I) and (II) being potentially distinct and not possessing the degree of convertibility corresponding with glutaconic mobility. Moreover, it was found by Perkin and Pickles that boiling the acid represented by (I) with potash or hydrochloric acid led to double-bond movement, the new acid being the Δ^3-form (V). In our experiments, also, during the attempted methylation of the Δ^2-ester in the presence of sodium methoxide, the ester recovered was that not of the Δ^2- but of the Δ^3-acid.

Such behaviour for a glutaconic acid is most unusual; all experience goes to show that the tendency for a glutaconic system to appear, even under apparently adverse conditions, is extremely strong. The disappearance of glutaconic properties occasioned by movement of the double bond outside the system is without parallel; indeed, the tendency is rather for the migration of a double bond to establish such a system (compare Farmer, J., 1923, **123**, 3324). In view of these facts, the correctness of Perkin and Pickles's allocation of formulæ appeared extremely doubtful, and in the hope that degradation of the supposed Δ^2-acid by ozone would give useful information, where Perkin and Pickles had found permanganate and nitric acid to fail, the oxidation of this substance was attempted by us. Among the oxidation products a considerable amount of tricarballylic acid was found. Such a product cannot arise from the true Δ^2-form, but only from the Δ^3- or Δ^4-form * as seen in the fission formulæ (VI), (VII), and (VIII).

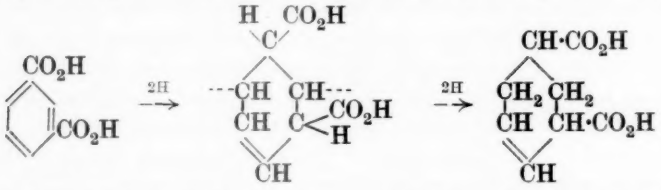
$\Delta^2 \longrightarrow HO_2C\cdot CO\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH(CO_2H)_2$ . . . . . (VI.)

$\Delta^3 \longrightarrow HO_2C\cdot CH_2\cdot CH_2\cdot CH(CO_2H)\cdot CH_2\cdot CO_2H$. . . . . (VII.)

$\Delta^4 \longrightarrow HO_2C\cdot CH_2\cdot CH(CO_2H)\cdot CH_2\cdot CH(CO_2H)_2$ . . . . (VIII.)

* We have been unable to complete the oxidation of the remaining isomerides or to apply other desirable tests owing to the exhaustion of our supply of material. A preliminary ozone oxidation of the *cis*-Δ^4-acid (P. and P.) yielded a considerable quantity of tricarballylic acid in accordance with the above scheme, but as the specimen employed did not, after numerous recrystallisations, quite attain the recorded melting point, it is intended to repeat the experiment.

There is little doubt, in view of the ease with which it yields an anhydride, that the Δ^2-acid of these authors is actually the *cis*-Δ^4-compound. Therefore the reduction of *iso*phthalic acid, which leads mainly to the production of this substance, may be represented thus:



It is hoped, when the further necessary evidence has been obtained, to investigate fully the properties of that isomeride possessing the glutaconic form.

Experimental.

*Tetrahydroisophthalic Acids.**—The *iso*phthalic acid required was obtained in large quantities by the prolonged boiling of commercial xylene with a sufficient excess of aqueous permanganate to ensure the absence of toluic acids. The mixture of *iso*phthalic and terephthalic acids obtained by decolorising, filtering, and acidifying the product was separated into its components by the usual barium salt procedure. Reduction of the *iso*phthalic acid was effected by the method of Perkin and Pickles (*loc. cit.*), as were also the isolation and, where necessary, the interconversion of the tetrahydro-acids. Most of the Δ^2-acid used in the experiments was obtained by hydrolysis of the pure Δ^2-anhydride. A portion, however, derived directly from the less soluble calcium salt was used : this was carefully compared with the acid from the anhydride before employment.

Ethyl Hydrogen Δ^2-Tetrahydroisophthalate.—The pure Δ^2-anhydride was refluxed for $3\frac{1}{2}$ hours with twice the quantity of ethyl alcohol theoretically necessary. The excess of alcohol was evaporated in a vacuum, and the product freed from neutral ester by means of sodium carbonate solution. Thorough cooling of the acidic portion caused partial crystallisation ; filtration and repetition of the process resulted finally in the separation of the material into a crystalline acid ester and an oil from which no further crystals could thus be separated. The solid crystallised from light petroleum in colourless prisms, m. p. 44—45° (Found : C, 60·6 ; H, 7·1 ; *M*, monobasic, 199. $C_{10}H_{14}O_4$ requires C, 60·6 ; H, 7·1% ; *M*, 198). The oily acid ester, the basicity of which indicated that some free acid was present, was distilled and collected in two fractions, b. p. 169—171° and 171—173°/1 mm. The first of these completely

* The description of compounds in the following pages is in accordance with the formulæ of Perkin and Pickles.

solidified on cooling; the second solidified but partly melted on resuming room temperature. The crystals from both specimens were identical and melted, after recrystallisation from light petroleum, at 40—41°. This substance was an acid ester, and was an isomeric form of that first isolated (mixed m. p. 31—37°) (Found: C, 60·4; H, 7·1%; *M*, monobasic, 197).

Methyl Hydrogen Δ^2-*Tetrahydroisophthalate.*—This substance also was obtained from the anhydride. As with *as*-dimethylsuccinic acid, whilst ethyl alcohol yields two distinct acid esters (J., 1904, **85**, 534; *Ann. Chim.*, 1923, **19**, 335), methyl alcohol gives only one recognisable form. The crude product, after removal of the excess of alcohol, solidified almost entirely. Systematic fractional recrystallisation from hexane resulted only in the isolation of one isomeride. The crystallisation liquors yielded on evaporation a small quantity of oil. Part of this was the dimethyl ester of the Δ^2-acid; the remaining acidic portion crystallised when isolated from the mixture and was identical with the form already obtained. Only a minute quantity of acidic material remained. The second isomeride, therefore, if formed, was present only in an unrecognisable amount. The acid ester crystallised in soft, flat prisms, m. p. 59° (Found: C, 58·6; H, 6·6; *M*, monobasic, 184. $C_9H_{12}O_4$ requires C, 58·6; H, 6·6%; *M*, 184). The pure, dry crystals, when kept for some time in an evacuated desiccator or in the air, invariably became oily on the surface. Whether this was the result of isomerisation, or other change, could not be determined.

Interconversion of the Isomeric Acid-esters.—The reaction between pure methyl hydrogen Δ^2-tetrahydro*iso*phthalate (1 mol.) and bromine (1 mol.) in dry chloroform did not appear to be a simple addition of bromine: decoloration was rapid, but there was no end-point to mark the absorption of one molecular proportion of the halogen. The product, after removal of chloroform, was a viscous, pale yellow oil from which the pure dibromide could not be obtained in the solid condition. This crude substance, although somewhat deficient in bromine, was treated in ethereal solution with an excess of diethylamine. Diethylamine hydrobromide separated rapidly, and from the colourless filtrate an almost colourless, viscous oil was isolated, which also could not be obtained in the solid condition. This crude substance, containing 80% of the bromine necessary for the pure bromotetrahydro*iso*phthalic acid ester, was reduced with zinc dust and acetic acid. The product was separated into a small neutral portion and a much larger acidic portion. The former solidified and yielded a neutral, difficultly crystallisable solid (rosettes of colourless needles, m. p. 41—43°), the nature of which has not been discovered. The acidic portion, after a small quantity of the

original acid ester had been removed, was distilled. The colourless distillate, b. p. 172—174°/1 mm., after a further very small quantity of the original easily crystallisable acid ester had been frozen out, remained liquid at room temperature. This substance, although not obtained in sufficient quantity to allow of adequate fractional distillation, approximated closely in composition and basicity to methyl hydrogen tetrahydro*iso*phthalate, and yielded the correct acid on hydrolysis. It distilled as a colourless oil, and is believed to represent the second isomeric form of the acid ester (Found: C, 59·8; H, 6·5%).

Methyl Δ^2*-tetrahydroisophthalate* was obtained by the action of methyl iodide on the silver salt of the pure acid. The crude ester (after removal of a small quantity of the above-described solid acid ester by washing with sodium carbonate solution) was obtained on distillation as a colourless oil, b. p. 134—135°/7 mm. (Found: C, 60·45; H, 7·1. $C_{10}H_{14}O_4$ requires C, 60·5; H, 7·1%). To ensure that isomeric change had not taken place during esterification, a small portion of the ester was rapidly hydrolysed with dilute sulphuric acid; only the Δ^2-acid could be isolated. The *amide*, which was readily obtained when the ester stood for 12 hours with concentrated aqueous ammonia at 40°, crystallised from water in flat prisms, m. p. 239°.

Methylation Experiments.—To the deep yellow solution obtained by mixing methyl Δ^2-tetrahydro*iso*phthalate with an equimolecular proportion of cold alcoholic sodium methoxide, an excess of methyl iodide was added. The temperature of the mixture rose somewhat, but as no change was apparent after 1½ hours, the mixture was heated for 4 hours on a steam-bath. The product isolated in the usual way consisted of a trace of acidic oil and a neutral ester that passed over on the first distillation at 138—143°/7 mm. On redistillation, almost the whole was obtained as a colourless oil, b. p. 140—141°/7 mm. This material was *methyl* Δ^3*-tetrahydroisophthalate*, since on rapid hydrolysis with dilute sulphuric acid it yielded, not the Δ^2-acid, but an acid identical in all respects with Perkin and Pickles's Δ^3-acid. Unlike the Δ^2-ester, this isomeride did not yield a comparatively insoluble amide on standing with aqueous ammonia (Found: C, 60·4; H, 7·1. $C_{10}H_{14}O_4$ requires C, 60·5; H, 7·1%).

When the methylation mixture, prepared as above, was heated at 120—130° for 5 hours in a sealed tube, the same Δ^3-ester was obtained in good yield. In neither case could any methylated product be isolated. Attempts to secure methylation by the use of sodium and methyl iodide failed because finely-pulverised sodium was not appreciably affected by solutions of the Δ^2-ester in ether and xylene, even on prolonged refluxing.

Attempted Preparation of the Hydroxy-anhydride.—(*a*) Following the method of Thole and Thorpe (J., 1911, **92**, 2236), the pure Δ^2-acid was heated in a sealed tube with an excess of acetyl chloride for 6 hours at 110°. The product, consisting of a small amount of a white powder and a brown liquid, was freed from acetyl chloride and dissolved in dry ether. The ethereal solution was rapidly shaken with an excess of sodium bicarbonate solution, and the alkaline extract immediately acidified. The resulting aqueous solution was found on extraction to contain an acid which was largely precipitated on removal of the bulk of the solvent; the ethereal mother-liquor contained a very small amount of a more soluble crystalline solid. These were identified by direct comparison with authentic specimens as Δ^3-tetrahydro*iso*phthalic acid (m. p. 243°) and the anhydride of the corresponding Δ^2-acid (m. p. 78°), respectively. No trace of the hydroxy- or chloro-anhydride could be isolated. The aqueous mother-liquor from the recrystallisation of the Δ^3-acid contained a small amount of material, m. p. 165—205°, probably a mixture of the Δ^2- and Δ^3-acids. (*b*) The pure anhydride of the Δ^2-acid (m. p. 78°) was heated as directed by Thole and Thorpe (*loc. cit.*) for 15 minutes at 150°. There was no apparent decomposition and the melt, when recrystallised from ether, was found to consist entirely of the unchanged anhydride. More vigorous heating of the anhydride (15 minutes) at 300—310° resulted in considerable darkening in colour. From an ethereal solution of the cooled melt, crystals of unchanged anhydride were deposited, the mother-liquor yielding on evaporation a solid melting indefinitely at 72—187°. This was redissolved in ether and separated rapidly, as above, into neutral and acidic portions. The neutral portion was unchanged anhydride; the acidic portion, m. p. 225—235°, had none of the characteristics of a hydroxy-anhydride and was separated by fractional crystallisation from water into two portions, identified by direct comparison with authentic specimens as Δ^3- and Δ^2-tetrahydro*iso*phthalic acids. A portion of the melt insoluble in ether consisted partly of the Δ^3-acid and partly of resinous material from which no solid material could be obtained.

The possibility that the Δ^3-acid was formed by the fission of a hydroxy-anhydride under the conditions used for separation (use of aqueous sodium bicarbonate) seems discounted by the absence of the characteristics of such a compound in the various fractions obtained by use of non-aqueous solvents.

Oxidation of Δ^2-Tetrahydroisophthalic Acid.—The acid derived from the pure Δ^2-anhydride (2½ g.) was dissolved in water and neutralised with a slight excess of sodium carbonate solution. A rapid stream of ozonised air was passed through the solution for

about 12 hours. The product, after being freed from ozone by the passage of a rapid current of air, gave a strong aldehyde reaction with Schiff's reagent. It was accordingly cooled to 0° and treated with 3% permanganate solution (equivalent to 1 atom of oxygen based on the quantity of substance taken). The cold product was filtered, acidified, and extracted with pure ether. The mother-liquor, to which the aqueous extract of the manganese mud was added, was concentrated on the steam-bath and the evaporation completed in a vacuum. The residue was thoroughly extracted, first with ether, then with acetone. Each of the ethereal extracts yielded a syrupy acid which largely solidified. The bulk of the solid material (about 1 g.), after being thoroughly washed with dry ether and twice recrystallised from ether, was readily identified as tricarballylic acid, m. p. 163°. The ether washings and acetone extract contained other acids, the nature of which has not yet been ascertained.

Ozonisation of the Δ^2-acid was also conducted in chloroform suspension, but, owing to the insolubility of the acid, oxidation was extremely slow. The product, after being decomposed with water and the solvent removed, was freed as far as possible from the unchanged acid and kept for 3 days with hydrogen peroxide. The product was then evaporated almost to dryness several times with water and finally freed from water. From the syrupy residue, a quantity of impure tricarballylic acid slowly crystallised.

We desire to express our gratitude for grants from the Government Grant Committee of the Royal Society (to E.H.F.) and the Chemical Society (to H.L.R.) which have defrayed a considerable portion of the cost of the research.

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LONDON, S.W. 7. [*Received, May 21st*, 1926.]

CCLXXXVIII.—*The Oxidation of Tartaric Acid by Solutions of Silver Salts.*

By DURBAN ROY MAXTED.

IT was shown by Claus (*Ber.*, 1875, **8**, 950) that when tartaric acid is oxidised with ammoniacal silver nitrate the resulting solution contains oxalic acid, and that the oxalic acid does not account for the whole of the tartaric acid used. It is now shown that when an excess (6—8 mols.) of silver nitrate is used the solution slowly deposits 6 atoms of silver per mol. of tartaric acid. In addition to

the oxalic acid, formic acid, carbon dioxide, and water are formed in quantities agreeing with the equations

$$C_4H_6O_6 + 3Ag_2O \longrightarrow 2(CO_2H)_2 + 6Ag + H_2O \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$
$$C_4H_6O_6 + 3Ag_2O \longrightarrow (CO_2H)_2 + H{\cdot}CO_2H + CO_2 + 6Ag + H_2O \quad (2)$$
$$C_4H_6O_6 + 3Ag_2O \longrightarrow 2H{\cdot}CO_2H + 2CO_2 + 6Ag + H_2O \quad . \quad . \quad (3)$$

The quantity of oxalic formed varies considerably according to the conditions. Temperature and dilution have no very marked effect, but the chief variation is caused by the concentration of alkali. The concentration of ammonia cannot be varied greatly, since it is restricted, on the one hand by the amount necessary to effect solution, and on the other by the fact that too much ammonia makes the reaction inconveniently slow. In the experiments in Table I the reaction mixture consisted of 20 c.c. of *N*/10-sodium tartrate and 63 c.c. of *N*/10-silver nitrate, to which was added the volume of *N*-ammonia shown in the table. The last column gives the number of mols. of oxalic acid obtained from one mol. of tartaric acid.

TABLE I.

Expt.	C.c. of *N*-ammonia.	Mols. of oxalic acid.
1	8	0·4150
2	12	0·5139
3	13	0·5885
4	15	0·7260
5	16	(Incomplete after one week.)

TABLE II.

Expt.	C.c. of *N*-NaOH.	C.c. of *N*-NH_3.	Mols. of oxalic acid.
3	—	13	0·5885
6	1	14	0·8932
7	2	19·5	1·318
8	4	23·5	1·410
9	6	24	1·468
10	8	28·3	(Incomplete.)

The alkalinity of the solution can be further increased by the addition of caustic soda. This causes the precipitation of silver oxide and necessitates the addition of larger quantities of ammonia. The reaction takes place readily, however, in the presence of quantities of ammonia which would inhibit it in the absence of the caustic soda. The marked increase in the quantity of oxalic acid produced in this way is shown in Table II.

The increase in the yield of oxalic acid is due more to the caustic soda than to the ammonia. This is demonstrated by Expts. 4 and 6: each had 15 c.c. of *N*-alkali, but in Expt. 6 the substitution of 1 c.c. of caustic soda for 1 c.c. of ammonia caused an increase of 23% in the yield of oxalic acid.

The Course of the Reaction.

The first attack of the tartaric acid might take place by:

(*a*) Splitting off one terminal carbon atom.

(*b*) Splitting off the two terminal carbon atoms symmetrically.

(*c*) Symmetrical rupture at the central bond.

(*d*) Oxidation to and subsequent rupture of dihydroxytartaric acid.

(*a*) With α-hydroxy-acids generally, oxidation with ammoniacal silver nitrate takes place readily, giving rise to carbon dioxide and the lower acid. When mandelic acid was used in this way, there was a distinct odour of benzaldehyde, showing that the aldehyde of the lower acid is an intermediate stage. It appears that with α-hydroxy-aldehydes oxidation with silver salts splits off the terminal carbon atom as formic acid. This is shown with aldoses such as glucose, where formic acid is the chief product of the reaction (Tollens, *Ber.*, 1883, **16**, 921). Then with an αβ-dihydroxy-acid we should expect the following changes :

$$\mathrm{R{\cdot}CH(OH){\cdot}CH(OH){\cdot}CO_2H \longrightarrow R{\cdot}CH(OH){\cdot}CHO + CO_2}$$
$$\longrightarrow \mathrm{R{\cdot}CHO + H{\cdot}CO_2H + CO_2}.$$

In this way, tartaric acid would give carbon dioxide, formic acid, and glyoxylic acid. Glyoxylic acid in this reaction is found to give oxalic and formic acids and carbon dioxide, the last two being in equimolecular proportions. The complete change following this course would agree with equations (2) and (3).

(*b*) If the tartaric acid were split as above at both ends of the molecule, we should have

$$\mathrm{C_4H_6O_6 \longrightarrow CHO{\cdot}CHO + 2CO_2}.$$

Glyoxal was tried in the reaction, however, and required 4 mols. of silver nitrate, producing no oxalic acid but equimolecular quantities of formic and carbonic acids. This would require the deposition of 8 atoms of silver instead of 6 for the complete reaction.

(*c*) Symmetrical rupture at the central bond, without previous oxidation to dihydroxytartaric acid, would probably first give 2 mols. of glyoxylic acid, each of which would oxidise, partly to oxalic acid, and partly to formic and carbonic acids : this would agree with equations (1) and (3).

(*d*) If dihydroxytartaric acid were an intermediate stage in the reaction, its further oxidation should require 2 mols. of silver nitrate ; it was found, however, to deposit quantities of silver varying from 2·3 to 5·4 atoms per mol. of the acid used.

Hence changes (*b*) and (*d*) are ruled out, leaving as the possible courses of the reaction :

$$\mathrm{C_4H_6O_6} \begin{cases} \nearrow \mathrm{CO_2 + CHO{\cdot}CH(OH){\cdot}CO_2H \longrightarrow CHO{\cdot}CO_2H + H{\cdot}CO_2H} \\ & \qquad \downarrow \searrow \mathrm{(CO_2H)_2} \\ \searrow \mathrm{2CHO{\cdot}CO_2H} \begin{cases} \nearrow \mathrm{2CO_2 + 2H{\cdot}CO_2H} \\ \searrow \mathrm{2(CO_2H)_2} \end{cases} & \mathrm{CO_2 + H{\cdot}CO_2H} \end{cases}$$

Experimental.

The substance to be oxidised was generally used in $N/10$-solution. The required quantity of the solution was mixed with the silver nitrate and ammonia in a conical flask which was connected to a long U-tube containing mercury to prevent loss of ammonia during the reaction. The flask was heated in a water-bath, usually at 60—62°. In most cases, 48 hours sufficed to complete the reaction, but when a large excess of ammonia was used the heating had to be continued for a further two or three days.

Analysis.—The silver deposited was filtered off and washed, first with water, then with ammonia, to remove any silver oxide or oxalate; thereafter it was dissolved in nitric acid and estimated with standard potassium thiocyanate. The filtrate and washings from the silver were treated at the boiling point with calcium nitrate solution. The precipitated calcium oxalate was dissolved in dilute sulphuric acid and titrated with standard permanganate.

To estimate the formic acid it was found necessary to remove the excess of silver left in the solution. This was done by adding sulphuric acid to the filtrate from the calcium oxalate and saturating the acid solution with hydrogen sulphide. The silver sulphide was filtered off and washed, and the filtrate and washings were left on the water-bath at about 70° until all the hydrogen sulphide had been driven off. Sodium carbonate was then added in excess, and the heating continued on the steam-bath until all the ammonia had been removed. A known excess of standard permanganate was then added (sufficient to give a purple solution), and the mixture left on the water-bath for 20 minutes. After acidification with sulphuric acid, the excess of permanganate was estimated by means of standard oxalic acid. Test experiments carried out with formic acid solutions of known strength showed that this method gave results usually 1—2% low, some formic acid probably escaping during the expulsion of the hydrogen sulphide. It was necessary to remove ammonia before the oxidation of the formic acid, otherwise the results varied between wide limits.

An estimation of carbon dioxide was carried out to show that the products of the reaction are formed in quantities agreeing with equations (1), (2), and (3). The reaction mixture consisted of 40 c.c. of $N/10$-tartaric acid, 125 c.c. of $N/10$-silver nitrate, and 23·1 c.c. of N-ammonia. All solutions were made with boiled-out water and the ammonia was freshly prepared by distillation from strong ammonia solution to which lime had been added. After the completion of the reaction, the solution was filtered as quickly as possible and made up to 250 c.c. In 100 c.c. of this solution, the

oxalic and formic acids were estimated as described above. Another 100 c.c. portion was acidified with sulphuric acid and distilled into 20 c.c. of standard caustic soda. Carbon dioxide and some formic acid passed over in the distillate. The total acid distilled was estimated by titrating the excess of caustic soda with standard sulphuric acid. The indicator used was the minimum quantity of phenolphthalein dissolved in boiling water without alcohol. The formic acid was estimated by alkaline oxidation with permanganate, as described above. One mol. of tartaric acid gave 0·8859 mol. of oxalic acid, 1·099 mols. of formic acid, and 1·118 mols. of carbon dioxide. [For equations (1), (2), and (3), 0·8859 mol. of oxalic acid require 1·1142 mols. each of formic acid and carbon dioxide.]

Glyoxal.—A solution of glyoxal (B.D.H.) was made containing approximately 0·1 mol. per litre. This solution was estimated with alkaline permanganate as in the case of formic acid (Found : oxalic acid, nil; Ag, 3·889, 4·149 atoms per mol. of glyoxal).

Glyoxylic Acid.—The calcium salt was prepared by the method of Debus (*Annalen*, 1856, **100**, 2). It was treated with sulphuric acid and distilled in steam. The acid in the distillate was estimated with baryta. Oxidation with ammoniacal silver nitrate gave, per mol. of glyoxylic acid : Silver, 1·997 atoms; oxalic acid, 0·1712 mol.; formic acid, 0·8165 mol.

Dihydroxytartaric Acid.—The sodium salt was washed ten times with water, well pressed, and dried in a vacuum desiccator. The dried salt was weighed out and mixed with water in a measuring flask. The mixture was well cooled and sufficient nitric acid added to dissolve the salt. When it was treated with ammoniacal silver nitrate, a black precipitate formed immediately. The mixture was left for some hours at the temperature of the laboratory in order to avoid heating unchanged dihydroxytartaric acid. The reaction was completed by heating for 2 days at 65°. The quantity of silver deposited varied considerably, but in each case was greater than 2 atoms per mol. of the original salt. Found, per mol. of dihydroxytartaric acid :

Silver	5·44	2·4	4·2 atoms.
Oxalic acid	0·226	1·895	0·435 mols.

The author wishes to express his thanks to The British Dyestuffs Corporation, Ltd., for supplying the sodium dihydroxytartrate, and to Professor H. Bassett for suggesting this work and for valuable assistance during its progress.

THE UNIVERSITY, READING. [*Received, May 29th*, 1926.]

CCLXXXIX.—*A New Method of Diagnosing Potential Optical Activity. Part II. The Optical Activity of Chlorobromoacetic Acid.*

By JOHN READ and ANN MORTIMER MCMATH.

CHLOROBROMOACETIC acid was first isolated in 1923 by Vanderstichele (J., **123**, 1225), and no attempts to resolve it into optically active components have been recorded. Vanderstichele's method consists in adding water to chlorobromoacetyl chloride, prepared by the elegant method of Crompton and Triffitt (*ibid.*, 1921, **119**, 1874) from αβ-dichlorovinyl ethyl ether. Since the acid is stated to undergo some decomposition during the subsequent distillation, it appeared desirable to devise an alternative process which would lead directly to the pure anhydrous acid, starting preferably from chlorobromomalonic acid. Although the diethyl ester of the latter acid has been described (*Ber.*, 1891, **24**, 2995), its saponification would be impracticable owing to the reactivity of the associated halogen elements. By the successive action of bromine and sulphuryl chloride upon a solution of malonic acid in dry ether, it was found possible, however, to prepare chlorobromomalonic acid in practically quantitative yield. When maintained at 130°, chlorobromomalonic acid is converted quantitatively into chlorobromoacetic acid, melting at 38°, this being 15° higher than the value recorded by Vanderstichele (*loc. cit.*). A new and expeditious method of proceeding from malonic acid to chlorobromomalonic and chlorobromoacetic acids is thus rendered available, and we propose in due course to undertake a detailed study of these interesting substances and certain of their derivatives.

All attempts to resolve chlorobromoacetic acid into optically active components by the use of brucine, in accordance with the customary methods, were unsuccessful. Similarly, upon fractionally crystallising the *l*-hydroxyhydrindamine salt from ethyl acetate, a homogeneous separation, consisting of transparent plates, was obtained.

Slow deposition of the salt from a dilute solution in cold chloroform containing a small proportion of dry methyl alcohol also yielded a homogeneous separation of transparent plates, identical with the salt deposited from ethyl acetate.

Rapid crystallisation during the cooling of a hot supersaturated solution in chloroform led, however, to a remarkably different result, an initial separation of soft, silky needles, equivalent in weight to the bulk of the original material, being succeeded by the slow formation of a relatively small amount of the transparent plates

mentioned above. The two kinds of crystals were isomeric and interconvertible; they showed little difference in melting point, and possessed practically the same optical rotatory power when dissolved in dry methyl alcohol or acetone.

A solution of the plates in chloroform containing dry methyl alcohol gave $[M]_D$ −50°, whilst the corresponding value in glacial acetic acid was −62°; no change in the optical rotation was noticed in either instance upon keeping or warming the solutions. The needles, however, behaved in a widely different manner when dissolved in these two solvents. In the first solvent no appreciable optical rotation was exhibited by a freshly-prepared solution, but on heating and keeping the solution, the rotation rose gradually to the value, $[M]_D$ −50°, given by the plates. In glacial acetic acid, the solution gave an initial value of $[M]_D$ −32°, which rose upon heating to −58°, this value also being identical with the rotatory power of the plates in the same solvent.

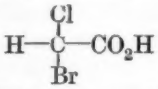
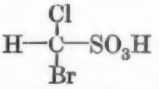
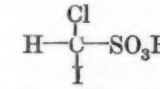
These relationships may be explained on the assumption that the plates and needles consist, respectively, of *l*-hydroxyhydrindamine *dl*-chlorobromoacetate (*l*B*dl*A) and *l*-hydroxyhydrindamine *d*-chlorobromoacetate (*l*B*d*A). The identical values of $[M]_D$ given by the two salts when dissolved in methyl alcohol or acetone must then be regarded as characteristic of the partly racemic salt, *l*B*dl*A; this conclusion is supported by the approximate coincidence of the values in question with those determined for *l*-hydroxyhydrindamine dichloroacetate under similar conditions. It appears, therefore, that the salt *l*B*d*A undergoes a rapid partial racemisation to *l*B*dl*A when dissolved in acetone or methyl alcohol. In the case of chlorobromomethanesulphonic acid (J., 1925, **127**, 1572), a similar change occurs slowly in methyl alcohol, whilst in acetone a disturbed equilibrium is attained between the diastereoisomeric salts *l*B*d*A (19%) and *l*B*l*A (81%).

The racemising action of methyl alcohol is suppressed to some extent by dilution with chloroform, so that when dissolved at the ordinary temperature in chloroform containing a little dry methyl alcohol, the salt *l*B*d*A appears to be optically stable. Owing to the opposed optical rotatory effects of the basic and acidic components, the salt has no measurable optical activity in this solvent. Upon heating, the racemising action of the methyl alcohol contained in the solution is enhanced, with the result that the optical rotation characteristic of the salt *l*B*dl*A is slowly attained. A closely similar effect is produced in glacial acetic acid.

It is only in chloroform containing not more than a trace of methyl alcohol that the existence of a disturbed equilibrium of the type *l*B*d*A $\rightleftharpoons$ *l*B*l*A can be presumed from the observations recorded below.

In a hot concentrated solution of this kind, the tabular salt *l*B*dl*A passes into such an equilibrium mixture, in which the salt *l*B*d*A obviously predominates, since the first crystalline deposit, formed to the extent of 75% or more on cooling, consists of needles of this salt. The diastereoisomeric salt *l*B*l*A cannot be isolated, the only other substance deposited by the mother-liquor being the partly racemic salt *l*B*dl*A. The total optical rotatory effect of the material receives a substantial increment in the positive sense as a result of the conversion of the salt *l*B*dl*A to *l*B*d*A. The reverse conversion of *l*B*d*A to *l*B*dl*A occurs at once on dissolving the first of these salts in methyl alcohol; the resulting partly racemic salt then remains practically unaffected by the subsequent addition of chloroform and crystallisation at the ordinary temperature.

Comparing the above observations with those recently recorded for chlorobromomethanesulphonic acid (*loc. cit.*), it may be concluded that the mobility of the atoms H, Cl, Br, and the group CO_2H, associated with the asymmetric carbon atom of configuration (I), is markedly greater than that of the same three atoms and the group SO_3H attached to the sole carbon atom of configuration (II):

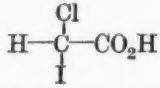
(I.)  (II.)  (III.) 

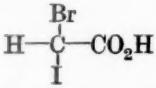
Chlorobromoacetic acid. Chlorobromomethanesulphonic acid. Chloroiodomethanesulphonic acid.

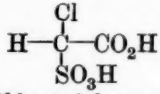
Moreover, it has already been demonstrated (*loc. cit.*) that configuration (II) is exceedingly more mobile in this respect than configuration (III). In the three systems indicated, the mobility is thus lessened by the substitution of (*a*) SO_3H for CO_2H, and (*b*) I for Br. The anticipation (*loc. cit.*, p. 1583) that certain asymmetric compounds containing two carbon atoms in the molecule would prove capable of giving rise in suitable solvents to a dynamic equilibrium between diastereoisomeric salts is thus justified, and it is shown that an asymmetric two-carbon atom molecule may, indeed, possess a more pronounced optical mobility than an appropriate closely related one-carbon atom molecule. The great mobility of configuration (I) is emphasised further by the fact that when the optically active acid was brought into combination with *dl*-hydroxyhydrindamine, by mixing equal weights of the salts *d*B*l*A and *l*B*dl*A in chloroform solution, the initial optical activity disappeared in a few minutes, whereas with configuration (II) the acid retained its activity for about 30 hours in similar circumstances (*loc. cit.*, p. 1581).

From the results just reviewed it may now be anticipated that chloroiodoacetic acid (IV) and bromoiodoacetic acid (V) will probably exhibit an optical stability less than that of (III) above, and

possibly of the same order as chlorosulphoacetic acid (VI), which, according to Backer and Burgers (J., 1925, **127**, 233), racemises only slowly in cold aqueous solution. This aspect of the research is receiving attention.

(IV.)  Chloroiodoacetic acid.

 (V.) Bromoiodoacetic acid.

 (VI.) Chlorosulphoacetic acid.

It is noteworthy that in the present instance the lævorotatory base favours a dextrorotatory orientation of the acid, and thus it appears that no general statement is possible in cases of this kind concerning the sense of the optical rotation imposed by the resolving agent upon the mobile asymmetric system with which it is associated (compare *loc. cit.*, p. 1583).

The data brought forward above afford an indication that the values of $[M]_D$ observed for the needles in cold chloroform and glacial acetic acid are to be attributed to the pure salt *l*B*d*A, rather than to an equilibrium mixture. By subtracting the corresponding values for the tabular salt *l*B*dl*A, an approximate expression is obtained for the molecular rotation exerted by the acid part of the first molecule in the solvent concerned (*loc. cit.*, p. 1577). The values are thus $+50°$ in chloroform and $+30°$ in glacial acetic acid; the corresponding values for configurations (II) and (III) in the latter solvent are $+125°$ and $+46°$, respectively, but no data can be determined for chloroform in these instances, owing to the insolubility of the salts concerned.

In general, the investigation of the optical activity of chlorobromoacetic acid is rendered difficult owing to the very limited number of suitable solvents, the sparing solubility and darkening of the optically active salts in these solvents, the small polarimetric readings, and the exceeding sensitiveness of the mobile asymmetric system.

An attempted partial asymmetric synthesis of an optically active chlorobromoacetic acid by heating the acid brucine salt of chlorobromomalonic acid to 130° yielded brucine *dl*-chlorobromoacetate (compare Marckwald, *Ber.*, 1904, **37**, 349); this result is in keeping with the last of the factors mentioned in the preceding paragraph.

In our first communication (*loc. cit.*, p. 1584), it was indicated that the salts of chlorobromomethanesulphonic acid with the optically active hydroxyhydrindamines provided a new and highly-refined means of testing certain aspects of the problem of complete asymmetric synthesis. In accordance with this conception, experiments have been devised to ascertain the possibility of disturbing the

delicate optical equilibrium *l*B*l*A $\rightleftharpoons$ *l*B*d*A existing in acetone solution by submitting the solution to certain external agencies which have been deemed to possess an asymmetric directive influence on chemical processes (compare van 't Hoff, "Die Lagerung der Atome im Raume," 1894, p. 30; Cotton, *Ann. Chim.*, 1896, **8**, 373; Byk, *Z. physikal. Chem.*, 1904, **49**, 641; McKenzie and Walker, J., 1922, **121**, 349). The equilibrium, however, remained unaffected when the solution was exposed to a beam of plane or circularly polarised (mercury green) monochromatic light in a magnetic field (367 *C.G.S.* units), and a similar result attended the use of a solution of the salt *l*B*dl*A in dry methyl alcohol. These experiments, although fruitless, appear worthy of record, as affording a stronger indication than has hitherto been forthcoming of the impracticability of achieving a complete asymmetric synthesis by means of the agencies in question. We propose, in due course, to carry out a number of still more refined experiments, with the aim of investigating the conceivable exertion by such agencies of an accelerative or delaying influence upon the attainment of optical equilibria in instances of the kind under notice.

Experimental.

Preparation of Chlorobromomalonic Acid and Chlorobromoacetic Acid.—An ice-cooled solution of malonic acid (52 g.) in dry ether (200 c.c.) was treated gradually with bromine (27 c.c.; 1 mol.); at the end of the reaction sulphuryl chloride (46 c.c.; somewhat more than 1 mol.) was added slowly. The product, after drying for 6 days over calcium chloride and sodium hydroxide in a slow current of dry air, crystallised in long, transparent prisms. Crystallisation was inhibited by admitting moist air or by diminishing the pressure within the desiccator. The crude material was purified by cautiously adding light petroleum to a strong solution in dry ether: the resulting hard, glittering needles gave analytical results corresponding to anhydrous chlorobromomalonic acid, and melted at 138° when heated rapidly.

Chlorobromomalonic acid, which is very deliquescent, dissolves readily in water, alcohol, or ether. It decomposes with evolution of carbon dioxide at temperatures much exceeding 100°; in aqueous solution, a corresponding effervescence sets in well below 100°, and in a vacuum a similar change appears to take place slowly at the ordinary temperature, particularly with impure specimens of the substance.

The normal *brucine* salt was very sparingly soluble in water and in the ordinary organic solvents. The acid *brucine* salt was sparingly soluble in water or ethyl acetate; it dissolved readily in alcohol,

acetone, or chloroform, and was insoluble in ether. A solution in chloroform ($c = 0{\cdot}70$) had $[\alpha]_D$ $-15{\cdot}2°$, and showed no mutarotation.

Chlorobromoacetic acid, $CHClBr{\cdot}CO_2H$, was obtained by heating chlorobromomalonic acid at 130° until the evolution of carbon dioxide was complete. The resulting colourless liquid crystallised on cooling, forming fine needles, which, drained on porous plate, melted at 38°. The substance is extremely deliquescent and it dissolves readily in water, alcohol, acetone, or ether (Found: *M*, by titration, 177. $C_2H_2O_2ClBr$ requires *M*, 173·5). When heated under reflux for an hour with an excess of *N*/10-sodium hydroxide, the acid suffered hydrolysis of the halogen elements to the extent of 66%. It is thus far less stable in this respect than chlorobromomethanesulphonic acid (J., 1925, **127**, 1585).

Experiments on the Optical Resolution of Chlorobromoacetic Acid.—1. *Brucine chlorobromoacetate*, prepared from its components by fractional precipitation from acetone, forms minute needles. It is very sparingly soluble in water and in most of the usual organic solvents, with the exception of chloroform, in which it is appreciably soluble in the cold. An almost saturated solution in chloroform, containing 0·2528 g. in 20·0 c.c., gave α_D $-0{\cdot}43°$ in a 2-dcm. tube, whence $[\alpha]_D$ $-17{\cdot}0°$. No mutarotation was observed, and the successive fractions of the salt gave practically identical values. An elaborate series of fractional precipitations from methyl alcohol led to a similar result. The brucine salt was also fractionally precipitated by adding successive quantities of a warm aqueous solution of brucine hydrochloride to a similar solution of ammonium chlorobromoacetate, but no appreciable difference was observed in the rotatory powers of the various fractions, which resembled in every respect the fractions prepared from the organic solvents mentioned above. The brucine salt also appeared to be homogeneous after repeated recrystallisation from boiling methyl alcohol.

An unsuccessful attempt to effect a partial asymmetric synthesis was made by heating the acid brucine salt of chlorobromomalonic acid to 130° with a little nitrobenzene, until the evolution of carbon dioxide was complete. The resulting clear solution deposited crystals of brucine chlorobromoacetate on cooling, and a further amount of this salt was precipitated from the mother-liquor on the addition of ether. In its optical rotatory power and other characteristics, the product was identical with the salt prepared in the other ways just described.

2. l-*Hydroxyhydrindamine* dl-*chlorobromoacetate*. Chlorobromoacetic acid was mixed in acetone solution with an equivalent weight of *l*-hydroxyhydrindamine, the resulting salt being isolated by evaporating the solution to dryness and washing the crystalline

residue with dry ether. Owing to the ready solubility of the salt in acetone and methyl alcohol, it was recrystallised from warm ethyl acetate. The transparent plates prepared in this way melted with decomposition at 165°. Further purification was effected by redissolving the salt in a small quantity of warm, dry methyl alcohol and adding about 25 times the volume of chloroform. Crystallisation began in about 2 hours and was complete in 24 hours. The product consisted of well-developed plates of rectangular appearance, the average length of side being 3 or 4 mm., and the thickness about 1 mm. M. p. 165°. The salt is almost insoluble in pure chloroform (Found: C, 40·2; H, 4·0. $C_{11}H_{13}O_3NClBr$ requires C, 40·6; H, 4·0%).

A solution of 0·2518 g. of the salt in pure dry methyl alcohol made up to 20 c.c. gave the constant value α_D −0·50° in a 2-dcm. tube, whence $[\alpha]_D$ −20·0° and $[M]_D$ −65°. The corresponding initial values in pure dry acetone were $[\alpha]_D$ −56° and $[M]_D$ −182°. A slow downward mutarotation similar to that exhibited by *d*-hydroxyhydrindamine acetate, etc., occurred when this solution was kept (compare J., 1912, **101**, 759, 777; 1925, **127**, 1575). l-*Hydroxyhydrindamine dichloroacetate*, which crystallised from warm acetone containing methyl alcohol in small, glittering prisms, m. p. 139°, gave $[M]_D$ −195° in acetone, and showed a closely similar mutarotation. This salt gave the constant value $[\alpha]_D$ −24·6°, $[M]_D$ −68°, in pure dry methyl alcohol (Found: C, 47·2; H, 4·3. $C_{11}H_{13}O_3NCl_2$ requires C, 47·5; H, 4·7%). Repeated attempts to obtain a second form of crystalline separation of *l*-hydroxyhydrindamine dichloroacetate by varying the conditions of crystallisation were unavailing.

l-*Hydroxyhydrindamine* d-*chlorobromoacetate*. *l*-Hydroxyhydrindamine *dl*-chlorobromoacetate was dissolved with the aid of heat in the minimum amount of dry methyl alcohol, to which was then added about 20 times the volume of chloroform. The solution was concentrated to approximately half bulk on a boiling water-bath, so as to remove practically all the methyl alcohol. Rapid crystallisation set in upon then allowing the resulting supersaturated solution in chloroform to cool, and the liquid became permeated with radiating aggregates of soft, silky needles, averaging about 1 cm. in length. After the lapse of an hour or so, crystalline plates characteristic of *l*-hydroxyhydrindamine *dl*-chlorobromoacetate began to separate; accordingly in most of the subsequent operations the needles were separated from the mother-liquor about 20 minutes after crystallisation had begun. When washed with chloroform and dried, the needles melted with decomposition at about 157°. The yield amounted to 75% or more of the weight of the original salt,

depending upon the precise conditions adopted. The salt is almost insoluble in pure chloroform. It was found possible to transform the needles of the *d*-chlorobromoacetate to the tabular *dl*-chlorobromoacetate, and *vice versâ*, at will, by observing the conditions of crystallisation described above. The two substances gave practically identical results when analysed by combustion.

When dissolved in pure dry acetone, by warming, and examined under the conditions indicated above, *l*-hydroxyhydrindamine *d*-chlorobromoacetate gave an initial value of $[M]_D$ −178°, declining to −129° after 36 hours, with darkening of the solution. In pure dry methyl alcohol a constant value of $[M]_D$ −64° was observed. In these respects, the salt was practically indistinguishable from *l*-hydroxyhydrindamine *dl*-chlorobromoacetate.

Polarimetric Discrimination between l-*Hydroxyhydrindamine* dl-*Chlorobromoacetate and* l-*Hydroxyhydrindamine* d-*Chlorobromoacetate.*—1. Upon dissolving 0·1032 g. of *l*-hydroxyhydrindamine *dl*-chlorobromoacetate (plates) at the ordinary temperature in a mixture of chloroform with about one-twentieth of its volume of dry methyl alcohol, and making the solution up to 20·0 c.c., the value α_D −0·16° was observed in a 2-dcm. tube, whence $[\alpha]_D$ −15·5° and $[M]_D$ −50°. No change in rotation was observed on keeping or heating this solution.

A similar determination made with *l*-hydroxyhydrindamine *d*-chlorobromoacetate (needles) revealed the absence of any measurable optical rotation under the conditions noted. After heating the solution for 20 minutes on the water-bath, the value $[M]_D$ −38° was observed, and upon keeping the solution at the ordinary temperature for a further 12 hours the value rose to −50°. As in (2) below, precise measurements of mutarotation were rendered difficult through the darkening of the solution.

2. A solution in glacial acetic acid containing 0·2024 g. of *l*-hydroxyhydrindamine *dl*-chlorobromoacetate (plates) made up to 20·0 c.c. at the ordinary temperature, gave α_D −0·40° in a 2-dcm. tube, whence $[\alpha]_D$ −19·7° and $[M]_D$ −62°. The reading remained unaltered after keeping the solution or heating it on the water-bath.

A similar solution of *l*-hydroxyhydrindamine *d*-chlorobromoacetate (needles), which had been purified by four successive recrystallisations, gave an original value $[M]_D$ −32°, which rose to −50° after heating for 20 minutes on the water-bath and to −58° after heating for a further 2 minutes over a small flame. The weight of salt used in this experiment was 0·2001 g., the actual successive readings of α_D observed in the polarimeter being −0·20°, −0·31°, and −0·36°. All the operations described under (1) and (2) were carried out in duplicate without any sensible difference being noticed in the

results. The concentrations adopted were practically the highest attainable at the ordinary temperature.

3. For purposes of control, similar observations were made upon solutions of *l*-hydroxyhydrindamine dichloroacetate. The values in chloroform containing dry methyl alcohol were $[\alpha]_D$ −16·6°, $[M]_D$ −46°, and in glacial acetic acid $[\alpha]_D$ −24·7°, $[M]_D$ −68°. In both instances, the optical rotation remained constant on heating or keeping the solutions.

Exhibition of Optical Activity by Chlorobromoacetic Acid in Combination with an Optically Inactive Base.—1. A solution of β-naphthylamine acetate in glacial acetic acid failed to give a precipitate or separation when added to solutions of the *d*- or *dl*-chlorobromoacetate of *l*-hydroxyhydrindamine in the same solvent, and the replacement of acetic acid by chloroform led to no more satisfactory result. Similar experiments with other symmetric bases demonstrated the impracticability of transferring the chlorobromoacetic acid to combination with such a base, so as to produce a salt possessing the requisite range of solubility.

2. Upon using *d*-hydroxyhydrindamine in place of the *l*-base, it was found possible to prepare specimens of *d*-hydroxyhydrindamine *dl*-chlorobromoacetate (plates) and *d*-hydroxyhydrindamine *l*-chlorobromoacetate (needles), by applying the methods described above. These salts behaved in every way as the respective enantiomers of the salts already discussed, and showed the corresponding optical rotatory powers, mutarotation, etc. In order to bring *l*-chlorobromoacetic acid into combination with *dl*-hydroxyhydrindamine, a mixture of 0·2014 g. of *d*-hydroxyhydrindamine *l*-chlorobromoacetate and 0·2014 g. of *l*-hydroxyhydrindamine *dl*-chlorobromoacetate was dissolved rapidly to 20·0 c.c. in chloroform containing a little dry methyl alcohol. The value of α_D observed 1·5 minutes after the first contact of the solid with the solvent was about −0·1°, and within the course of a further minute or so the solution became completely inactive. In the absence of racemisation, the calculated value of α_D for the conditions adopted is about −0·3°. Two similar experiments were carried out with glacial acetic acid as a solvent; in these instances, 4 to 5 minutes elapsed before a polarimetric reading could be taken, and no optical activity could be established.

We express our acknowledgments to the Department of Scientific and Industrial Research for a maintenance grant which enabled one of the authors (A. M. M.) to take part in the investigation, which is being continued.

UNITED COLLEGE OF ST. SALVATOR AND ST. LEONARD,
UNIVERSITY OF ST. ANDREWS. [*Received, May 17th,* 1926.

CCXC.—*The Optical Resolution of Chlorosulphoacetic Acid.*

By JOHN READ and ANN MORTIMER MCMATH.

WITH the exception of chlorobromoacetic acid (preceding paper), chlorosulphoacetic acid is the sole substance containing only two carbon atoms in the molecule whose ability to exist in enantiomorphous modifications has been satisfactorily demonstrated. Following inconclusive attempts to resolve chlorosulphoacetic acid with the aid of alkaloids and of *d*-hydroxyhydrindamine (Pope and Read, J., 1908, **93**, 795; 1914, **105**, 814), optically active aqueous solutions of ammonium *d*- and *l*-chlorosulphoacetate were recently prepared by Backer and Burgers (J., 1925, **127**, 233). These authors adopted the method of repeated fractional deposition of an alkaloidal salt from cold water. Aqueous solutions of ammonium *d*-chlorosulphoacetate prepared by decomposing two such fractions of a strychnine salt in the cold, with the calculated quantity of ammonia, exhibited the values $[M]_D$ +18·7° and +20·5°, respectively, the latter value being the highest recorded. Similarly, by the use of cinchonine, an aqueous solution of ammonium *l*-chlorosulphoacetate having the maximum value $[M]_D$ −18·5° was obtained. These solutions manifested a slow decline in optical rotatory power when kept, and the ammonium salt racemised completely when evaporated to dryness.

From our related investigations it appeared that a substance so susceptible to racemisation in aqueous solution could scarcely be obtained in optically pure enantiomorphous modifications by means of the procedure adopted by Backer and Burgers (compare J., 1925, **127**, 1573, footnote). These anticipations were borne out as a result of a careful examination of the behaviour in organic solvents of the normal salt of chlorosulphoacetic acid with *l*-hydroxyhydrindamine. By fractional crystallisation from cold dry methyl alcohol, this salt readily yielded pure *l*-hydroxyhydrindamine *d*-chlorosulphoacetate, whilst the very soluble diastereoisomeric salt, *l*-hydroxyhydrindamine *l*-chlorosulphoacetate, remained in the mother-liquor, in association with a certain amount of the first salt. Upon converting *l*-hydroxyhydrindamine *d*-chlorosulphoacetate, *via* the sparingly soluble brucine salt, into ammonium *d*-chlorosulphoacetate, the value $[M]_D$ +31° was observed for the last-named salt in dilute aqueous solution, in agreement with the approximate value $[M]_D$ +36° calculated from the rotation of *l*-hydroxyhydrindamine *d*-chlorosulphoacetate. The result is in keeping with the comparatively low molecular rotatory powers recorded in our preceding

communications for related substances of simple molecular constitution. On account of the impracticability of recrystallising the impure *l*-hydroxyhydrindamine *l*-chlorosulphoacetate obtained from the mother-liquors, the maximum rotatory power exhibited by the derived ammonium *l*-chlorosulphoacetate was only $[M]_D$ −24°.

Backer and Burgers noticed that free *d*-chlorosulphoacetic acid, prepared by adding the calculated quantity of dilute sulphuric acid to an aqueous solution of ammonium *d*-chlorosulphoacetate having $[M]_D$ +20·5°, showed the much higher value $[M]_D$ +40°. The ammonium salt now described, having $[M]_D$ +31°, yielded in a corresponding way *d*-chlorosulphoacetic acid having $[M]_D$ +76°, the enhanced rotatory power being thus even more pronounced. Conversely, the value $[M]_D$ +53° of a partly racemised acid fell to $[M]_D$ +16° after exact neutralisation with ammonia.

According to Backer and Burgers, aqueous solutions of *d*-chlorosulphoacetic acid and ammonium *d*-chlorosulphoacetate underwent complete racemisation when evaporated to dryness. We have succeeded, however, in preparing crystalline specimens of optically active ammonium and benzidine salts of chlorosulphoacetic acid. Upon evaporation to dryness of an aqueous solution of pure ammonium *d*-chlorosulphoacetate, the value of $[M]_D$ rose from +31° to +60°. The optical activity gradually declined to the original value in about 12 hours, and complete racemisation occurred upon then evaporating the solution to dryness; in this instance, the second solution possessed only one-quarter of the concentration of the original solution. Further experiments indicated that complete racemisation attends the slow evaporation of dilute solutions of the optically active ammonium salts, whereas the racemisation is partly or completely masked during the rapid evaporation of stronger solutions. Since the residual material after evaporation to dryness gave no evidence of appreciable hydrolysis, elimination of ammonium chloride, or other chemical change, an indication is afforded of the possible existence of ammonium *d*-chlorosulphoacetate in two dynamically isomeric forms possessing different rotatory powers, the free acid being apparently related more immediately to the ammonium salt possessing the higher optical activity than to the other. Each of the *l*-hydroxyhydrindamine salts, *l*B*d*A and *l*B*l*A, exhibited corresponding changes upon evaporation to dryness, the values of $[M]_D$ changing from −85° to −61° and −81° to −111°, respectively. Thus, the optical rotatory powers of the ions of the *d*- and *l*-acid apparently received respective increments of 24 and 30 units as a result of the process.

The previous failure to effect the resolution of this acid by means of *d*-hydroxyhydrindamine (J., 1914, **105**, 814) must be attributed

to the racemising action of the water present in the hot aqueous alcohol used as solvent; the slight yet distinct fall in the molecular rotatory powers of successive fractions indicates that a partial resolution had indeed taken place, as suggested at the time. Since it is now shown that brucine *l*-chlorosulphoacetate is much less soluble in methyl alcohol than its diastereoisomeride, it appears likely that resolution might also be effected by means of a fractional separation of the brucine salts from this solvent, and we hope to investigate this point more fully.

Experimental.

dl-*Chlorosulphoacetic Acid*, $CHCl(SO_3H)\cdot CO_2H$.—The barium salt (80 g.), prepared by Andreasch's method (*Monatsh.*, 1887, **7**, 159), was fractionally crystallised from hot water (2000 c.c.), the recrystallised first fraction being taken as pure (Found: Ba, 41·5. C_2HO_5ClSBa,H_2O requires Ba, 41·9%). A suspension of the finely-powdered salt in hot water was treated with the requisite quantity of *N*-sulphuric acid, the concentration of chlorosulphoacetic acid in the filtered solution being then ascertained by titration.

Salts of d-*Chlorosulphoacetic Acid.*

l-*Hydroxyhydrindamine* d-*Chlorosulphoacetate*, $2C_9H_{11}ON,C_2H_3O_5ClS$.—Upon mixing equivalent weights of *dl*-chlorosulphoacetic acid (8·7 g.) and *l*-hydroxyhydrindamine (14·9 g.) in dry methyl alcohol (300 c.c.), the cold solution deposited a first fraction (4·2 g.) composed of minute, glistening prisms, m. p. 203° (decomp.); 0·2002 g., in solution (20·0 c.c.) in dry methyl alcohol, gave α_D −0·36° in a 2-dcm. tube, whence $[\alpha]_D$ −18·0° and $[M]_D$ −85°. No mutarotation was observed on keeping this solution for 2 days. In a similar way, the mother-liquor yielded three further fractions, all of which were identical with the first fraction in appearance, rotatory power and melting point. The combined fractions, amounting to somewhat more than 40% of the calculated weight of one of the diastereoisomeric salts, underwent no appreciable alteration when fractionally recrystallised from dry methyl alcohol in the same way. The substance was therefore regarded as pure l-*hydroxyhydrindamine* d-*chlorosulphoacetate* (Found: C, 50·4; H, 4·9. $C_{20}H_{25}O_7N_2ClS$ requires C, 50·8; H, 5·3%).

The salt dissolves readily in water, fairly readily in warm methyl alcohol, less readily in ethyl alcohol or glacial acetic acid, and is only sparingly soluble in most of the other common organic solvents. When a solution in dry methyl alcohol was evaporated to dryness on the water-bath and the *l*-hydroxyhydrindamine *d*-chlorosulpho-

acetate then redissolved in the cold solvent, the original values $[\alpha]_D$ −18·0°, $[M]_D$ −85° declined to $[\alpha]_D$ −12·5°, $[M]_D$ −59°. In water, 0·2001 g. made up to 20·0 c.c., gave α_D −0·36° in a 2-dcm. tube, whence $[\alpha]_D$ −18·0° and $[M]_D$ −85°. No mutarotation was observed on keeping this solution for 2 days, but upon evaporating it to dryness on the water-bath and redissolving the crystalline residue in cold water, the observed value for the solution, made up to 20 c.c., was α_D −0·26°, whence $[\alpha]_D$ −13·0° and $[M]_D$ −61°. Upon dissolving 0·1350 g. of the salt similarly in glacial acetic acid, with gentle warming, the values α_D −0·26°, $[\alpha]_D$ −19·2°, $[M]_D$ −91° were recorded, but no observations of possible mutarotation could be made, owing to the rapid crystallisation of the material in the polarimeter tube.

Brucine d-*Chlorosulphoacetate*.—To a cold solution of *l*-hydroxyhydrindamine *d*-chlorosulphoacetate (1·4 g.) in water (40 c.c.) was added a solution of the calculated weight of brucine (2·8 g.) in water (30 c.c.) containing a corresponding quantity of hydrochloric acid. Brucine *d*-chlorosulphoacetate (2·4 g.) was deposited slowly as hard, glistening prisms, with an average length of about 5 mm. The salt, m. p. 196° (slight decomp.), is sparingly soluble in water, glacial acetic acid, or chloroform, but it dissolves readily in methyl alcohol. A solution in methyl alcohol, containing 0·2036 g. in 20·0 c.c., gave α_D −0·04°, whence $[\alpha]_D$ −2°.

Ammonium d-*Chlorosulphoacetate*, $CHCl(SO_3NH_4)\cdot CO\cdot ONH_4,H_2O$. —To an aqueous suspension of powdered brucine *d*-chlorosulphoacetate (about 4 g.) was added gradually at the ordinary temperature the calculated quantity of *N*-ammonia, together with a little chloroform, admixture being effected by shaking. The chloroform solution of the alkaloid was removed, and the aqueous layer extracted three times with the same solvent. The neutral aqueous solution, made up forthwith to 20·0 c.c., gave α_{5461} +1·20° and α_D +1·02° ($l = 2$). By subsequently evaporating an aliquot part of the aqueous solution to dryness, the total weight of ammonium salt ($M = 226·5$) present in 20·0 c.c. was found to be 0·7376 g., whence $[\alpha]_{5461}$ +16·3°, $[M]_{5461}$ +37°, and $[\alpha]_D$ +13·8°, $[M]_D$ +31°; the rotatory dispersion Hg_{5461}/Na_D is thus 1·177. These readings remained unaltered after the solution had been kept for 24 hours.

5 C.c. of the solution were rapidly evaporated to dryness on a boiling water-bath, the crystalline residue being finally dried in a steam-oven. The resulting 0·1844 g. of ammonium salt, when redissolved in cold water, made up to 20·0 c.c., gave at once α_D +0·49° ($l = 2$), whence $[\alpha]_D$ +26·6° and $[M]_D$ +60°, and α_D +0·35°, +0·29°, and +0·24° after 8 minutes, 6 hours, and 12 hours, respectively, the corresponding values of $[M]_D$ being +43°, +36°,

and +29°. The solution was then evaporated to dryness; the crystalline residue when redissolved in water exhibited no measurable optical activity.

Another measured volume (10·0 c.c.) of the original solution of ammonium *d*-chlorosulphoacetate, having $[M]_D$ +31°, was treated with the calculated quantity of *N*-sulphuric acid (2 equivs.) and made up to 20·0 c.c. with water. The solution, containing 0·2841 g. of *d*-chlorosulphoacetic acid, gave α_D +1·24° ($l = 2$), whence the values $[\alpha]_D$ +43·6° and $[M]_D$ +76° are derived for the free acid in dilute aqueous solution containing ammonium sulphate. When the solution was boiled for ½ minute and cooled rapidly, the reading α_D fell to +1·02°, whence $[\alpha]_D$ +35·8° and $[M]_D$ +62°; after 18 hours, the value α_D +0·87° was observed, corresponding to $[\alpha]_D$ +30·5° and $[M]_D$ +53°. The solution was finally treated with the calculated quantity of *N*-ammonia and made up to 30·0 c.c. with water; α_D was then +0·17°, so that the dissolved ammonium *d*-chlorosulphoacetate had $[\alpha]_D$ +6·9° and $[M]_D$ +16°.

Ammonium *d*-chlorosulphoacetate crystallises in hard, glistening needles. It dissolves readily in water, but is practically insoluble in alcohol or acetone. An aqueous solution was rapidly evaporated to dryness, and the crystalline residue washed with methyl alcohol; it then decomposed at 207°. Ammonium *dl*-chlorosulphoacetate, after similar treatment, decomposed at 201°. In each instance, the redissolved salt gave only a slight opalescence when treated with dilute nitric acid and silver nitrate. Ammonium *d*-chlorosulphoacetate, obtained in the manner indicated, appears to resemble barium *dl*-chlorosulphoacetate and free chlorosulphoacetic acid by containing one molecular proportion of combined water (Found: NH_3, by absorption in standard acid, 14·7. $C_2H_9O_5N_2ClS,H_2O$ requires NH_3, 15·0%). A similar statement applies to ammonium *dl*-chlorosulphoacetate, which gave identical analytical results.

Benzidine d-*chlorosulphoacetate* separated in almost quantitative yield upon mixing solutions in glacial acetic acid of *l*-hydroxyhydrindamine *d*-chlorosulphoacetate and benzidine acetate. The salt is practically insoluble in the usual organic solvents, but it dissolves appreciably in hot water, from which the racemised salt separates, on cooling, in long, glistening needles, decomposing at 245°. Owing to its sparing solubility in cold water, the optical activity of the original separation was established by examining an almost saturated solution in a 4-dcm. tube in mercury green light. A solution containing 0·0858 g. in 30·0 c.c. gave α_{5461} +0·18°, whence $[\alpha]_{5461}$ +15·7°. The optical activity slowly diminished, and vanished when the solution was evaporated to dryness.

Salts of l-*Chlorosulphoacetic Acid.*

l-*Hydroxyhydrindamine* l-*Chlorosulphoacetate.*—The mother-liquor from the fourth fraction of *l*-hydroxyhydrindamine *d*-chlorosulphoacetate, described above, when kept at the ordinary temperature for several days yielded a somewhat sticky, semi-solid mass; this became dry and pulverable after further keeping in a desiccator. From the method of preparation, the material evidently consisted of *l*-hydroxyhydrindamine *l*-chlorosulphoacetate contaminated with a certain amount of *l*-hydroxyhydrindamine *d*-chlorosulphoacetate; owing, however, to its ready solubility and its reluctance to crystallise, a satisfactory purification of the salt was impracticable. When made up to 20·0 c.c. in dry methyl alcohol, 0·2004 g. gave α_D −0·48° ($l = 2$), whence $[\alpha]_D$ −24·0° and $[M]_D$ −113°. Similarly, for 0·2001 g. in water, the value observed was α_D −0·34°, whence $[\alpha]_D$ −17·0° and $[M]_D$ −81°. The residue obtained by evaporating this solution to dryness gave the following values when redissolved in cold water and made up again to 20·0 c.c. : α_D −0·47°, $[\alpha]_D$ −23·5°, $[M]_D$ −111°.

Brucine l-*Chlorosulphoacetate.*—The above *l*-hydroxyhydrindamine salt, when treated with brucine acetate in the manner already indicated, yielded a separation of small, colourless prisms, which decomposed slightly at 206° and completely at 235°, without melting. The material, which evidently consisted of brucine *l*-chlorosulphoacetate contaminated with the diastereoisomeric salt, differed from the latter by reason of its slight solubility in methyl alcohol; it was sparingly soluble in water, glacial acetic acid, or chloroform.

Ammonium l-*Chlorosulphoacetate.*—Crude brucine *l*-chlorosulphoacetate was decomposed with dilute ammonia in the manner described above. The resulting aqueous solution, containing 1·2601 g. of the ammonium salt in 30·0 c.c., gave α_D −0·74° ($l = 2$), whence $[\alpha]_D$ −9·6°, $[M]_D$ −20°. After 2 days, the values were α_D −0·61°, $[\alpha]_D$ −8·0°, $[M]_D$ −16·5°. When the solution was evaporated to dryness on the water-bath the optical activity vanished.

A specimen of the ammonium salt prepared from brucine *l*-chlorosulphoacetate which had been purified by extraction with boiling methyl alcohol had $[\alpha]_D$ −10·6° and $[M]_D$ −24°, the former being the highest specific rotation observed for ammonium *l*-chlorosulphoacetate.

An aqueous solution of another specimen of the ammonium salt, containing 1·3 g. in 20 c.c. and having $[M]_D$ −12°, was divided into two equal parts. On evaporating the first part to dryness as rapidly as possible on the water-bath, the value of $[M]_D$ declined to −8°; the second part, when evaporated similarly to a syrupy consistency, showed $[M]_D$ −11° when re-examined. The racemisation was

accelerated considerably in solutions containing small amounts of free ammonia.

The authors are indebted to the Department of Scientific and Industrial Research for a maintenance grant which enabled one of them (A. M. M.) to take part in this investigation.

UNITED COLLEGE OF ST. SALVATOR AND ST. LEONARD,
UNIVERSITY OF ST. ANDREWS. [*Received, May 26th*, 1926.]

CCXCI.—*The Action of Thionyl Chloride on Hydroxyanthraquinones. Part III.*

By ALBERT GREEN.

WHEN purpurin is treated with boiling thionyl chloride, two only of the three hydroxyl groups enter into reaction. The product contains one sulphite group, closely resembles thionylalizarin (J., 1924, **125**, 1450) in properties, and yields 2-acetylpurpurin when boiled with acetic acid. It is therefore 1 : 2-*thionylpurpurin* (I), and, like the alizarin analogue, it reacts rapidly with moisture, reverting to the hydroxy-compound.

In the case of anthrapurpurin all three hydroxyls are affected and 1 : 2-*thionyl*-7-*chlorothionylanthrapurpurin* (II) results. This is even less stable to moisture than the previously described compounds of this series, and is converted by acetic and benzoic acids into *monoacyl* derivatives, which, in view of the analogous formation of 2-monoacetyl derivatives of alizarin and of purpurin, must be formulated as 2-acyl-1 : 7-dihydroxyanthraquinones. With acetic anhydride, the chlorothionyl compound is quickly converted into triacetylanthrapurpurin.

The thionyl derivatives of hystazarin and anthragallol are differentiated from those above mentioned by their greater stability to moisture and by their different behaviour with acetic acid. These differences must be ascribed to the different positions of the sulphite groups. When boiled with acetic acid, *thionylhystazarin* (III) reverts completely to hystazarin, whilst 2 : 3-*thionylanthragallol* (IV) gives a mixture of anthragallol and a *monoacetylanthragallol*, which from considerations of steric hindrance is probably 3-*acetylanthragallol*.

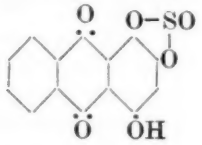
Thionylhystazarin also differs from the other thionyl derivatives of this series in that its conversion into diacetylhystazarin takes place with comparative slowness and is still uncompleted after its solution in acetic anhydride has been boiled for ½ hour.

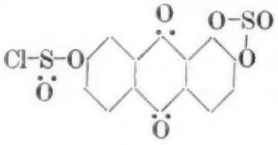
The structure of 2 : 3-thionylanthragallol is established on the evidence of its regulated interaction with acetic anhydride. Thionyl-

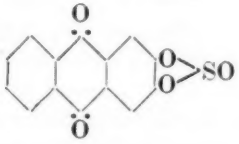
alizarin (*loc. cit.*) is quantitatively converted into diacetyl-alizarin by boiling its solution in acetic anhydride for 10 minutes; furthermore, Dimroth, Friedman, and Kammerer (*Ber.*, 1920, **53**, 481) have shown that 1-hydroxyl groups are scarcely affected when hydroxyanthraquinones are boiled with the anhydride for this time. When thionylanthragallol is so treated, a theoretical yield of 2 : 3-diacetylanthragallol results, and it is thus clear that the thionyl group is not linked to the 1-position of the anthragallol nucleus.

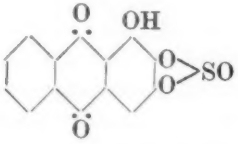
Anthraquinone, 1-hydroxyanthraquinone, 4- and 5-chloro-1-hydroxyanthraquinones, and 1 : 8-dihydroxyanthraquinone (chrysazin), are deposited unchanged from thionyl chloride, even after their solutions have been boiled for periods of 48 to 60 hours. 2-Hydroxyanthraquinone also does not react with boiling thionyl chloride, and it would appear, therefore, that in anthrapurpurin the 7-hydroxyl group, which is converted into a chlorothionyl group, is rendered more reactive by the presence of other hydroxyl groups as substituents in the second benzene nucleus.

The work described here and in Part I (*loc. cit.*) indicates that two ortho-hydroxyl groups in the anthraquinone series will always react with thionyl chloride to give a thionyl derivative: 1 : 2-thionyl compounds react with carboxylic acids, giving 2-acyl derivatives only; this rule does not hold when the thionyl group is attached to the 2 : 3-position.

(I.) 

 (II.)

(III.) 

 (IV.)

Since the melting points given in the literature for several of the hydroxy-compounds and for their acetyl derivatives are low, new data have been tabulated at the end of this paper.

Experimental.

The hydroxyanthraquinones were obtained by the hydrolysis of their pure acetyl derivatives with concentrated sulphuric acid (see Part II, this vol., p. 1428). *5-Chloro-1-hydroxyanthraquinone* was prepared from 5-amino-1-hydroxyanthraquinone by diazotisation. 1-Hydroxyanthraquinone and 2-hydroxyanthraquinone were

similarly obtained from the corresponding amines. All the acetyl derivatives were repeatedly crystallised from pyridine or pyridine–acetic anhydride.

The thionyl chloride was fractionated immediately before use.

Analyses.—On account of their instability, the thionyl compounds were analysed as soon as possible after preparation. Immediately before analysis the compounds were finely ground and heated for 20 minutes at 80—90° in order to remove traces of thionyl chloride and ether.

Thionylpurpurin (I).—Purpurin (10 g.) was boiled under reflux with 120 c.c. of thionyl chloride for 6 hours. The deep red solution was then concentrated to 50 c.c. and protected from moisture. Clusters of small, yellowish-brown crystals (8·5 g.) separated slowly; these were washed with absolute ether until free of thionyl chloride and stored in sealed tubes; m. p. 211—213° [Found: C, 55·3; H, 2·1; S, (*a*) by Carius's method, 10·6, and (*b*) iodometrically as sulphur dioxide produced by boiling with glacial acetic acid, 10·3; *M*, cryoscopic in naphthalene, 320, 325. $C_{14}H_6O_6S$ requires C, 55·6; H, 2·0; S, 10·6%; *M*, 302].

Thionylpurpurin is rapidly decomposed by moisture, and 0·7320 g., after standing in air for 24 hours followed by drying in a vacuum over sulphuric acid, yielded 0·6185 g. of purpurin (theory requires 0·6205 g.). This was recognised by conversion into the triacetate, by comparison with an authentic specimen (mixed melting point 256—258°), and by analysis (Found: C, 65·4; H, 3·2. Calc.: C, 65·6; H, 3·1%).

2-Acetylpurpurin was obtained by boiling 2·5 g. of thionylpurpurin with 50 c.c. of glacial acetic acid for 40 minutes. The cooled solution deposited 2·0 g. of orange-red crystals which, after recrystallisation from toluene, melted at 168—170° (Found: C, 64·5; H, 3·4; CH_3·CO, 14·0. Calc.: C, 64·4; H, 3·4; CH_3·CO, 14·4%).* The product was identical with that obtained by the monoacetylation of purpurin in pyridine.

1 : 2-*Thionyl*-7-*chlorothionylanthrapurpurin* (II).—Anthrapurpurin (10 g.) was boiled with thionyl chloride (200 c.c.) for 9 hours; the light red solution was concentrated to 30 c.c. and kept in the dry. The small, ochre-coloured crystals (14 g.) that separated were washed with dry benzene and absolute ether; they were very sparingly soluble in all common organic solvents and melted at 179° (decomp.) (Found: C, 43·9; H, 1·4; Cl, 9·3; S, 16·6. $C_{14}H_5O_7ClS_2$ requires C, 43·7; H, 1·3; Cl, 9·2; S, 16·6%). When 1·304 g. were kept in the air, decomposition occurred rapidly with

* When acetyl derivatives were sparingly soluble in alcohol, A. G. Perkin's device (J., 1925, **127**, 1886) of dissolving them in concentrated sulphuric acid before estimation by the ethyl acetate method, was adopted.

the evolution of fumes, and the product after drying was 0·924 g. of anthrapurpurin (theory requires 0·923 g.), which was recognised by a mixed melting-point determination and by analysis (Found : C, 65·6; H, 3·2. Calc. : C, 65·6; H, 3·1%).

2-*Acetylanthrapurpurin*, $C_{14}H_7O_5{\cdot}CO{\cdot}CH_3$.—The preceding compound (2 g.) was sifted into boiling glacial acetic acid (30 c.c.). Sulphur dioxide and hydrogen chloride were evolved, and yellow crystals (1·5 g.) of 2-*acetylanthrapurpurin* separated from the hot solution. These melted at 296—298° with charring, and this melting point was unchanged by further recrystallisation (Found : C, 64·2; H, 3·4; $CH_3{\cdot}CO$, 14·1. $C_{14}H_7O_5{\cdot}CO{\cdot}CH_3$ requires C, 64·4; H, 3·4; $CH_3{\cdot}CO$, 14·4%). When 0·70 g. of this product dissolved in hot pyridine was treated with 0·25 c.c. (2 mols.) of acetic anhydride, the red solution became pale yellow and on cooling deposited 0·79 g. of pure triacetylanthrapurpurin, which was identified by comparison with an authentic specimen.

2-*Benzoylanthrapurpurin*, $C_{14}H_7O_5{\cdot}CO{\cdot}C_6H_5$.—A mixture of 2·5 g. of the chlorothionyl compound and 2·0 g. of dry benzoic acid was heated at 170° until the evolution of gas ceased (about 10 minutes). The product was twice crystallised from tetrachloroethane, from which 2-*benzoylanthrapurpurin* separated in clusters of microscopic, yellow needles, m. p. 203—205° (Found : C, 70·2; H, 3·4. $C_{21}H_{12}O_6$ requires C, 70·0; H, 3·3%). The compound is sparingly soluble in boiling acetic acid or benzene, more soluble in hot toluene, and very soluble in boiling tetrachloroethane.

Triacetylanthrapurpurin.—The chlorothionyl compound (2·0 g.) was added slowly to boiling acetic anhydride (10 c.c.). After 15 minutes, the pale red solution was cooled and deposited 1·5 g. of triacetylanthrapurpurin as yellow plates, melting at 225—227° alone or when mixed with a pure specimen (Found : $CH_3{\cdot}CO$, 33·1. Calc. : $CH_3{\cdot}CO$, 33·0%).

Thionylhystazarin (III).—After boiling for 12 hours with 400 c.c. of thionyl chloride, 7 g. of hystazarin had dissolved to a red solution, which was concentrated to 50 c.c. The pale yellowish-green, rectangular plates which separated (6·8 g.; and 0·8 g. on further concentration of the filtrate) were filtered off rapidly and washed with absolute ether; m. p. 200° (Found : C, 58·5; H, 2·1; S, 11·0; *M*, cryoscopic in naphthalene, 295. $C_{14}H_6O_5S$ requires C, 58·7; H, 2·1; S, 11·2%; *M*, 286). After standing in moist air for 3 weeks, 0·249 g. gave, when dried, 0·214 g. (0·209 g. theoretical) of hystazarin (Found : C, 69·8; H, 3·4. Calc. : C, 70·0; H, 3·3%).

Interaction with Acetic Acid.—Thionylhystazarin (1·5 g.) was dissolved in 100 c.c. of boiling acetic acid, and yellow crystals soon began to separate. After 45 minutes, the solution was cooled and the crystals (1·2 g.) were collected. These contained no sulphur,

and were identified as hystazarin by comparison and by analysis (Found: C, 70·0; H, 3·1. Calc.: C, 70·0; H, 3·3%). The yellow precipitate obtained by stirring the filtrate into water apparently consisted of pure hystazarin only (Found: C, 69·8; H, 3·3%).

Diacetylhystazarin.—A solution of the thionyl compound in acetic anhydride was boiled for 1 hour. The fine, pale yellow needles obtained melted at 211—213°, alone and when mixed with pure diacetylhystazarin (Found: C, 66·5; H, 3·7; CH_3·CO, 26·3. Calc.: C, 66·7; H, 3·7; CH_3·CO, 26·5%). When recrystallised from pyridine, the substance was obtained as pale greenish-yellow plates with the same melting point.

2 : 3-*Thionylanthragallol* (IV).—When 4 g. of anthragallol * had been treated with 80 c.c. of boiling thionyl chloride for 1½ hours, a dark green solution was suddenly formed. After 5 hours' further boiling, the evolution of hydrogen chloride had almost ceased and the solution was concentrated to about 30 c.c. After 12 hours, slender, greenish-yellow rods (3·0 g.) of 2 : 3-*thionylanthragallol* were filtered off, and washed thoroughly with absolute ether. The filtrate on concentration yielded a further 0·7 g. The product, which was free from chlorine, melted at 218—220°, with previous slight sintering (Found: C, 55·4; H, 2·0; S, 10·6; *M*, in freezing naphthalene, 290, 300. $C_{14}H_6O_6S$ requires C, 55·6; H, 2·0; S, 10·6%; *M*, 302). After 0·3796 g. of the thionyl compound had been exposed to the air for 10 days, it yielded, when dried, 0·3208 g. (0·3218 g. theoretical) of anthragallol, m. p. 312—314° (Found: C, 65·4; H, 3·2. Calc.: C, 65·6; H, 3·1%).

2 : 3-*Diacetylanthragallol.*—Finely-powdered thionylanthragallol (2 g.) was sifted into boiling acetic anhydride (60 c.c.). The yellowish-green solution was boiled for 10 minutes and then rapidly stirred into ice-water. The yellow precipitate (2·4 g.) was washed with cold water. It melted at 213—216° and, after two crystallisations from pure acetone, at 223—224°, either alone or when mixed with authentic 2 : 3-diacetylanthragallol prepared by the partial acetylation of anthragallol in pyridine solution (Found: C, 63·3; H, 3·5; CH_3·CO, 25·4. Calc.: C, 63·5; H, 3·5; CH_3·CO, 25·3%).

Interaction of 2 : 3-*Thionylanthragallol with Acetic Acid.*—(A) *Anthragallol.*—In a typical preparation thionylanthragallol (1·65 g.) was boiled for 45 minutes with glacial acetic acid (160 c.c.). The red solution, after 2 days, deposited 0·55 g. of anthragallol as light brown spherules, m. p. 313—314° (Found: C, 65·5; H, 3·1. Calc.: C, 65·6; H, 3·1%). After concentration to 30 c.c., the filtrate yielded a further 0·45 g., m. p. 312—314° (Found: C, 65·6; H,

* Anthragallol was obtained from Anthracene Brown, W. by extraction with nitrobenzene. I am indebted to Professor A. G. Perkin, F.R.S., for informing me of this method.

3·2%). Both melting points were unchanged when the specimens were mixed with pure anthragallol.

(B) 3-*Monoacetylanthragallol*.—When the filtrate from the second crop of anthragallol was stirred into cold water, 0·55 g. of a golden-brown solid, m. p. 206—209°, separated, which crystallised from toluene in small, golden-brown rods, m. p. 210—212° (Found: C, 64·5; H, 3·2; CH_3·CO, 14·0. $C_{14}H_7O_5$·CO·CH_3 requires C, 64·4; H, 3·4; CH_3·CO, 14·4%).

5-*Chloro*-1-*hydroxyanthraquinone*.—A solution of 5-chloro-1-amino-anthraquinone (10 g.) in concentrated sulphuric acid (100 c.c.) was treated at 0° with powdered sodium nitrite (3·0 g.) during 1 hour and then stirred for 8 hours. On the next day, the mixture was heated at 130—140° for 5 minutes and poured into 2 litres of cold water; the resulting suspension was boiled and filtered. The bright yellow solid obtained was dissolved in 2% aqueous caustic soda, and the solution was filtered (to remove unchanged amine) into boiling hydrochloric acid. The golden-yellow product melted at 221—222°.

5-*Chloro*-1-*acetoxyanthraquinone*.—The hydroxy-compound was boiled with a mixture of acetic anhydride and pyridine. The *acetyl* compound formed crystallised from a similar mixture in pale primrose needles, m. p. 205° (Found: Cl, 11·6; CH_3·CO, 14·3. $C_{14}H_6O_3Cl$·CO·CH_3 requires Cl, 11·8; CH_3·CO, 14·3%). When hydrolysed by boiling with a solution of sulphuric acid in absolute alcohol, it gave 5-*chloro*-1-*hydroxyanthraquinone* in bright golden-yellow, rectangular plates, m. p. 223—224° (Found: C, 65·1; H, 2·8; Cl, 13·6. $C_{14}H_7O_3Cl$ requires C, 65·0; H, 2·7; Cl, 13·7%).

The melting points given below were determined with short-stemmed thermometers.

Hydroxy-compounds (crystallised from alcohol).	M. p.	Completely acetylated derivatives (crystallised from pyridine).	M. p.
1-Hydroxyanthraquinone, pale primrose needles.	191—192°	Small, pale primrose plates.	183—185°
2-Hydroxyanthraquinone, pale yellow needles.	305	Fine, stone-coloured needles.	160
4-Chloro-1-hydroxy-anthraquinone, golden-yellow needles.	193—194	Pale primrose needles.	176—177
Hystazarin.	—	Pale greenish-yellow plates.	211—213
Chrysazin, small, golden-yellow plates.	Orange-red at 160°, m. p. 193°.	Hexagonal, yellow plates.	244—245
Anthragallol, fine, orange-brown needles.	313—314	Very fine, yellow rods.	188—189
Purpurin, very fine, deep red needles.	257—259	Short, yellow rods.	203—205
Anthrapurpurin.	—	Pale yellow plates.	226—228

The author wishes to express his indebtedness to the Research Fund Committee of the Chemical Society, by whom a portion of the expenses of this research has been defrayed, and also to the following manufacturers for gifts of materials: The British Alizarine Company, Limited; I.G. Farbenindustrie Aktiengesellschaft, Leverkusen; and The Scottish Dyes, Limited.

THE EDWARD DAVIES LABORATORIES, UNIVERSITY COLLEGE OF WALES, ABERYSTWYTH. [*Received, May 17th*, 1926.]

CCXCII.—*Synthesis of Certain Higher Aliphatic Compounds. Part II. The Hydration of Stearolic Acid.*

By GERTRUDE MAUD ROBINSON and ROBERT ROBINSON.

ALTHOUGH the hydration of acetylenic acids such as stearolic, palmitolic, tariric, and behenolic acids has been carefully studied in connexion with the determination of the constitution of long-chain unsaturated acids, we have been unable to find any suggestion in the literature, apart from unsharp melting points, that mixtures are produced, for example, by successive treatment of the acids with sulphuric acid and with water. The synthesis of some of the pure keto-acids described in Part I (J., 1925, **127**, 175) gave rise to compounds exhibiting sharp melting points and the properties of 10-ketostearic acid made it evident that the product of hydration of stearolic acid is a mixture.

We have now synthesised 9-ketostearic acid,

$$CH_3 \cdot [CH_2]_8 \cdot CO \cdot [CH_2]_7 \cdot CO_2H,$$

by graduated hydrolysis of the condensation product from ethyl sodio-2-acetyl-*n*-decoate and 8-carbethoxy-*n*-octoyl chloride. Dr. G. Shearer kindly examined the reflexion of *X*-rays from specimens of 9-ketostearic acid, 10-ketostearic acid and the hydration product of stearolic acid. The distribution of intensity among the various orders of reflexion from the principal planes was found to be different for the two isomeric acids, whilst the stearolic-hydration product exhibited an intermediate character.

Analysis of the hydration product gave figures in close agreement with those required by the formula $C_{18}H_{34}O_3$, and we were encouraged in the laborious task of preparing sufficient pure 9- and 10-keto-stearic acids to render possible a thermal analysis of the mixture. This has been carried out and the results obtained show that the hydration product consists of 9- and 10-ketostearic acids and contains 42·4% of the former isomeride. The ratio of the velocity of

formation of 10-ketostearic acid to that of its isomeride is accordingly 1·36. Almost identical results were obtained by dissolving solid stearolic acid in sulphuric acid and by extracting the substance from a hexane solution by sulphuric acid. In view of the probability that the molecules of stearolic acid are oriented at the sulphuric acid–hexane surface and taking into consideration also the electrical field to which these molecules at the boundary would be subjected, some effect might have been anticipated. Its absence indicates that the hydration occurs in the body of the solution and is an event subsequent to the solution of the stearolic acid in the sulphuric acid. Analogous studies of the hydration products of palmitolic and behenolic acids are in progress.

The case of stearolic acid is almost unique in organic chemistry in the opportunity afforded for a comparison of the orienting effects of distant groups without complications due to conjugation. The lengths of the carbon chains on each side of the triple bond are equal, but the terminal group on one side is oxidised.

$$CH_3 \longrightarrow [CH_2]_7 - \overset{+}{C} \equiv \overset{-}{C} - [CH_2]_7 \longrightarrow CO_2H$$

We make a direct comparison of the general effects of methyl as against carboxyl. From another point of view, the terminal groups may be regarded as substituting hydrogen atoms. The nature of the electronic displacements anticipated theoretically as a result of the replacement of hydrogen by methyl and by carboxyl are indicated by the arrows in the above expression and it will be noticed that these are in the *same* direction. On account of the presence of the methyl group and the carboxyl group, therefore, the favoured direction of polarisation of the triple bond is that which will lead to a predominant production of 10-ketostearic acid. In the general case R·C:C·R′, the formation of R·CO·CH_2R′ should be favoured (*a*) by increasing the length of the hydrocarbon chain in R, (*b*) by branching of the chain in R, (*c*) by introducing into R′ groups such as CO_2H,NO_2,Cl, which tend to attract electrons more than H does, (*d*) by bringing such groups as CO_2H in R′ nearer to the triple bond.

As an illustration of the application of these principles, we may note that the disparity found in the case of stearolic acid, CH_3·$[CH_2]_7$·C:C·$[CH_2]_7$·CO_2H, should be increased in the same sense when we turn to palmitolic acid, CH_3·$[CH_2]_7$·C:C·$[CH_2]_5$·CO_2H. The carboxyl is nearer to the triple bond than it is in stearolic acid, and although the left-hand chain has not been lengthened, the right-hand chain is shorter than that in stearolic acid. Conversely, the disparity in the case of behenolic acid, CH_3·$[CH_2]_7$·C:C·$[CH_2]_{11}$·CO_2H,

should be less than in the case of stearolic acid, because the right-hand chain is longer and the carboxyl is further removed from the triple bond. The results obtained in these cases should provide a test of the validity of the theory. It is remarkable that the combined effects of the methyl and carboxyl in stearolic acid should be so powerful at such a distance from the reactive centre, and it is obviously unnecessary to look beyond general electron displacement (Lewis; Lucas) for an explanation of such phenomena as the direction of addition of hydrogen bromide to αβ-unsaturated acids.

We include in this communication an account of some new application of the synthetical method described in Part I of the series.

Experimental.

4-Ketomyristic Acid, $CH_3{\cdot}[CH_2]_9{\cdot}CO{\cdot}[CH_2]_2{\cdot}CO_2H$.—The yield of ethyl 2-acetyl-*n*-undecoate, b. p. 191°/42 mm., from *n*-nonyl iodide was 77%. The ester (28 g.) in ethereal solution was converted into its sodio-derivative by means of sodium powder (2·5 g.), and 3-carbomethoxypropionyl chloride (16 g.), dissolved in ether, was gradually introduced, with shaking and cooling. After 12 hours, the product was isolated, agitated with 4% aqueous potassium hydroxide for 20 hours, collected by means of ether from the acidified solution, boiled with 5% sulphuric acid (500 c.c.) for 4 hours, and the hydrolysis completed by boiling 4% aqueous potassium hydroxide (700 c.c.) during 48 hours. The acid was purified by conversion into the sodium salt (yield 6·2 g. or 26%). The substance was crystallised from methyl alcohol and then from light petroleum, separating in colourless plates, m. p. 87° (Found: C, 69·3; H, 10·7. $C_{14}H_{26}O_3$ requires C, 69·4; H, 10·7%). This acid was synthesised in order to facilitate the identification of an acid obtained by Clutterbuck and Raper (*Biochem. J.*, 1925, **9**, 395) by the oxidation of myristic acid. The *oxime* crystallises from benzene–light petroleum in colourless rhombohedra, m. p. 74°.

9-Ketostearic Acid, $CH_3{\cdot}[CH_2]_8{\cdot}CO{\cdot}[CH_2]_7{\cdot}CO_2H$.—Ethyl hydrogen azelate was obtained in 40% yield from ethyl azelate by a method based on that employed by Grün and Wirth (*Ber.*, 1922, **55**, 2207) for the semi-hydrolysis of ethyl sebacate. The substance has b. p. 198°/16 mm. and m. p. 32°. 8-Carbethoxy-*n*-octoyl chloride, b. p. 182°/29 mm., was obtained from the acid (16 g.) and thionyl chloride (50 g.) in 70% yield. An ethereal solution of the chloride (9·5 g.) was gradually added to a solution of ethyl sodio-2-acetyl-*n*-decoate (from 0·97 g. of granulated sodium and 9·3 g. of the ester) in ether (15 c.c.) and after ¾ hour the mixture was boiled for 10 minutes. The product, isolated before each operation, was successively hydrolysed by means of cold aqueous 5% potassium hydroxide

(300 c.c.) for 6 hours, boiling 5% sulphuric acid (200 c.c.) for 24 hours, and boiling 10% aqueous potassium hydroxide (100 c.c.) for 6 hours. After the acid hydrolysis, 1·5 g. of the ketostearic acid was isolated and in addition some methyl nonyl ketone, m. p. 13·5°; oxime, m. p. 46—47° (Spiegler, *Monatsh.*, 1884, **5**, 242, gives m. p. 42°; Thoms, *Ber. Deut. pharm. Ges.*, 1901, **2**, 3, gives m. p. 46—47°). The total yield of 9-ketostearic acid was 4 g. (36%). The sodium salt was crystallised from water; the recovered acid crystallised from alcohol in colourless plates, m. p. 83° (Found: C, 72·7; H, 11·7. Calc. for $C_{18}H_{34}O_3$: C, 72·5; H, 11·4%). This acid is very sparingly soluble in light petroleum and it is apparently identical with the ketostearic acid, m. p. 83°, which Behrend (*Ber.*, 1896, **29**, 807) obtained from 10-chloro-9-ketostearic acid by reduction with zinc and alcoholic acetic acid. The oily oxime was changed by sulphuric acid to an amide, m. p. 79° after crystallisation from methyl alcohol and from benzene (Behrend, *loc. cit.*, gives m. p. 75—85°). The corresponding compound from 10-ketostearic acid crystallises from benzene–light petroleum in colourless plates, m. p. 80°.

10-*Ketononadecoic Acid*, $CH_3{\cdot}[CH_2]_8{\cdot}CO{\cdot}[CH_2]_8{\cdot}CO_2H$.—The condensation of ethyl sodio-2-acetyl-*n*-decoate (from 26 g. of the ester) and 9-carbethoxy-*n*-nonoyl chloride (26 g.) and the subsequent hydrolysis of the product in stages were carried out in the usual manner. The final alkaline solution was acidified, steam-distilled for the separation of methyl nonyl ketone, and largely diluted with water. The oil solidified and the substance crystallised from methyl alcohol in colourless plates, m. p. 86—87° (yield, 5·6 g.) (Found: C, 72·8; H, 11·3. $C_{19}H_{36}O_3$ requires C, 73·1; H, 11·5%). This acid also crystallises well from ethyl acetate. Its oxime is converted by sulphuric acid into an *amide* crystallising from methyl alcohol in white plates, m. p. 83°.

This ketononadecoic acid was one of four similar substances submitted to Dr. G. Shearer for examination by *X*-ray methods (compare *Nature*, 1925, **116**, 45). Knowing only that the acids were of the form $CH_3{\cdot}[CH_2]_m{\cdot}CO{\cdot}[CH_2]_n{\cdot}CO_2H$, Dr. Shearer deduced from his observations not only the correct composition, but also the constitution of the substances. The interest of this achievement deserves to be emphasised, since it is the first of its kind to be recorded.

10-*Ketobehenic Acid*, $CH_3{\cdot}[CH_2]_{11}{\cdot}CO{\cdot}[CH_2]_8{\cdot}CO_2H$.—Ethyl 2-acetyl-*n*-tridecoate (26 g., 20% excess) was converted into its sodio-derivative in ethereal solution and condensed with 9-carbethoxy-*n*-nonoyl chloride (22 g.) in the usual manner. Hydrolysis of the product was carried out in stages as described in analogous cases, and the acid was finally freed from sebacic acid by means of hot

water. The yield was 32·6%, calculated on the acid chloride employed. The substance was purified through the sodium salt and then crystallised from methyl alcohol in colourless plates, m. p. 94° (Found : C, 74·3 ; H, 11·9. $C_{22}H_{42}O_3$ requires C, 74·6, H, 11·9%). The acid crystallises from light petroleum in diamond-shaped plates. Its oxime yields with sulphuric acid an *amide* crystallising from methyl alcohol in plates, m. p. 99°.

Mixtures of 9-Ketostearic Acid and 10-Ketostearic Acid.—The freezing points were determined in the usual manner * and with little difficulty except in the neighbourhood of the eutectic, where there is probably a double f. p. The thermometer could be read accurately to the nearest 0·01° and the mean of several closely-agreeing values was selected.

% of 9-Keto-stearic acid.	F. p.	% of 9-Keto-stearic acid.	F. p.	% of 9-Keto-stearic acid.	F. p.
0·0	80·14°†	38·07	72·19°	48·87	69·60°
16·31	77·17	40·39	71·50	50·35	69·59
29·51	74·31	41·88	70·99	55·65	69·73
30·86	73·99	42·85	70·65	58·72	70·89
32·66	73·61	45·20	69·97	60·33	71·40
35·96	72·77	47·18	69·63	64·21	72·42

† The m. p. of 10-ketostearic acid, taken very slowly in a capillary tube, is 82° (corr.). The f. p. is a value which is connected with the particular apparatus and method employed.

A smooth curve can be drawn through the points corresponding with the first eleven determinations, but near the eutectic there is a flat region.

Hydration of Stearolic Acid.—It was found in preliminary experiments that the composition of the hydration product was not appreciably modified by crystallisation of the mixture from light petroleum or by purification through the sodium salt. These methods were accordingly adopted in preparing specimens for analysis. The following examples may be given. Stearolic acid (3·8 g.) was dissolved in sulphuric acid (30 c.c.) and after 12 hours the mixture was added to ice. The acid was collected (3·4 g.) and converted into its sodium salt, which was crystallised from water (80 c.c.). The acid was then crystallised from 60 c.c. of light petroleum and dried at 100° (specimen A) (Found : C, 72·5, 72·3, 72·5, 72·4 ; H, 11·55, 11·3, 11·4, 11·4. Calc. for $C_{18}H_{34}O_3$: C, 72·5 ; H, 11·4%). A solution of stearolic acid (2 g.) in hexane (500 c.c.) was stirred with sulphuric acid (300 c.c.) for 4 hours. The sodium salt of the isolated acid was crystallised from 40 c.c. of water and the

* Compare Oxford and Robinson, this vol., p. 386. The values are uncorrected, but all details of the determinations were carefully standardised, this being of much greater importance in the present connexion than an accurate determination of the absolute f. p.

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